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LECTURE NOTES  
on  
QUALITATIVE ANALYSIS  
—  
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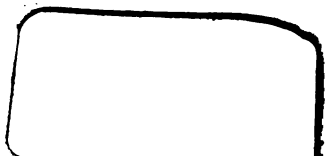
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LECTURE NOTES  
ON  
QUALITATIVE  
ANALYSIS

BY

HENRY B. HILL, A.M.

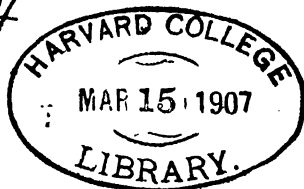
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*Gratis.*

## PREFACE.

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**ALTHOUGH** the advantages to be gained by teaching qualitative analysis by lecture are sufficiently obvious, it is a serious disadvantage to the student that the necessity of taking proper notes often prevents him from seeing what takes place upon the lecture table. This little book was intended to give concisely the most important facts essential to intelligent work in the laboratory, and thus give the student more leisure for observation in the lecture room.

A comparative description of those compounds of bases and acids which are commonly found or used in analysis is first given, and afterwards a method of separation which experience has proved to be sufficiently simple and accurate, is briefly explained. This method of procedure from the properties of compounds to the methods of separation will also serve to show the way in which the more difficult problems of analysis must be solved.

No tables for analysis have been given, since their use is of questionable advisability, and, if used, are much better drawn up by the student himself.

Symbols have been used throughout for reagents for the sake of brevity, those used in solution being distinguished by the addition of "Aq."

For the sake of simplicity, water has often been omitted from the formulae of compounds, inasmuch as the number of molecules of water

is largely dependent upon circumstances, and its presence is of minor importance.

Of a compilation of this sort, it is hardly necessary to add that its facts are taken mainly from the text-books of Fresenius and Rose, and the Dictionary of Solubilities of Storer.

CAMBRIDGE, Sept. 1, 1874.

## INTRODUCTION.

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**QUALITATIVE ANALYSIS** is that branch of chemistry which treats of the recognition of elements or their compounds. It demands a thorough study and comparison of the several elements and their compounds, of the phenomena exhibited by them under various conditions, and the determination of the particular conditions essential to the manifestation of each. It is advisable, at first, to take into consideration only the more common compounds, and to leave for subsequent study all rare elements and all but a few of the compounds of carbon (organic substances).

The phenomena exhibited by a substance under various conditions are termed its *reactions*. The conditions under which reactions are studied may be divided into two classes: those dependent upon solution, and those independent of it; the two modes of examination are known as the wet and the dry way. In either case any known substance which is used in effecting a reaction is called a *reagent*.

Reactions in the dry way are dependent upon volatilization, or chemical change effected by heat. The nature of these changes will be sufficiently clear after a study of the reactions described in the preliminary examination.

In the wet way a reagent is used to effect solution or to determine a metathesis. Experience has shown that when the solutions of two substances are mixed, and a compound insoluble under the existing conditions can be formed by metathesis, that this insoluble compound is formed; or when a substance volatile under the existing conditions can be formed, that it is formed and escapes. An insoluble substance

separating from solution is called a *precipitate*. If the precipitate settles readily, the liquid may be decanted, or, in any case, it may be separated by filtration, when the liquid is called the *filtrate*. Inasmuch as the completeness of the separation of those substances which are precipitated by a reagent from those which are left in solution depends upon the insolubility of the precipitate, all the conditions which may affect its solubility must be known and considered.

A *general reagent* is used to precipitate a number of substances, a *special reagent* as a test for a single substance. Some special reagents give no precipitate, but cause a change of color. The precipitate thrown down by a general reagent always requires further examination, and it is better to submit to a confirmatory test the precipitate caused by a special reagent. A precipitate or reaction is said to be characteristic when no further test is needed.

There are two things essential to success in qualitative analysis, the accurate observation of phenomena and a correct interpretation of their significance, neither of which can be attained without conscientious work in the laboratory. By studying the reactions of known substances, taking care to observe everything which takes place, however small it may seem, the power of observation will be educated, and it will soon be possible to determine what is accidental and what essential, and experience will show what is the meaning of each reaction observed.

In this book it is supposed that the student already has a good knowledge of general chemistry. Such knowledge is essential, and may be gained by the aid of any good text-book on chemistry. Experience in laboratory work and manipulation, though not absolutely necessary, is on all accounts desirable.\*

It is best to begin with the study of the bases, and, taking each group by itself, to compare the properties of the different members. The description of the properties of bases is intended as a guide

\* The student may be referred to the following text-books :—

PRINCIPLES OF CHEMICAL PHILOSOPHY. By Josiah P. Cooke, Jr. Boston, 1874.

A MANUAL OF INORGANIC CHEMISTRY : Arranged to facilitate the Experimental Demonstration of the Facts and Principles of the Science. By C. W. Eliot and F. H. Storer. New York, 1868.

INORGANIC CHEMISTRY. By T. E. Thorpe. New York, 1874.

in this work. The truth of each important fact given there should be experimentally proved, and reactions seen in the lecture-room should be repeated, if possible.

After a thorough study of the properties of a group of bases, a method of separation should be devised and compared with that given in course of analysis. The members of the group must then be separated from each other, taking care that the facts upon which the method of separation is based are well understood, and the sources of error distinctly recognized. The separation of the group as a whole from the other groups must then be considered, and the conditions necessary for complete separation clearly made out. After the basic groups have been studied in order, and each of the bases can be detected with certainty, a similar method should be followed with acids, taking as a guide the description of the properties of acids, and the methods given for their detection.

The student will then be prepared to make complete analyses. He should begin with simple salts, and proceed gradually to complex mixtures and insoluble substances, in every case proving the presence or absence of each base and acid which he has studied. In the analysis of such compounds the reactions in the dry way should first be observed. Here the significance of each reaction may be learned, as before, by practice upon known substances, or the reactions of a substance may be carefully observed, and its composition afterward determined by analysis in the wet way. The correct interpretation of reactions in the preliminary examination requires long practice. Great care must be taken to distinguish between those reactions which are so decisive that they may be taken as tests for the presence or absence of certain substances, and those which are proofs or indications of presence, if observed, but from whose non-appearance no negative conclusions can be drawn.

As far as practical work is concerned, it will be necessary to give here only a few general directions, and point out a few common errors. Neatness and cleanliness are absolutely necessary. The reagents must be carefully preserved from contamination. The stoppers of the bottles must not be misplaced, nor laid down while the reagent is used. The reagent bottles should



be kept clean and plainly labelled, they should be conveniently arranged, and the order of arrangement never changed.

The quantity of a substance taken for analysis should be small. This facilitates the manipulation, and unless carried to extreme, affords better practice.

Each reagent must be added cautiously, in quantity just sufficient. Too little fails to effect complete precipitation, and separation ; too much is often quite as objectionable. If the first few drops of a reagent cause a precipitate, more must be added until a drop allowed to run into the solution gives no further precipitate. The filtrate should also be tested with a few drops of the reagent in confirmation. In using an acid or an alkaline solution the reaction on test-paper will show when an excess has been added. In the use of a few reagents the necessary quantity can be learned by experience alone. In any case, the reagent must be thoroughly mixed with the solution by shaking or stirring.

If a solution is moderately concentrated, the precipitation is usually immediate ; but in dilute solutions it often takes place only after some time. If separation is to be effected, time should be allowed for complete precipitation. Occasionally half an hour, or even several hours, are necessary ; but more frequently five or ten minutes will be found sufficient. Heat almost always facilitates precipitation ; in a few cases, however, which are mentioned in the course of analysis, a reagent must be used in the cold.

In filtering, the filter must be evenly folded and carefully fitted to the funnel. For rapid filtration a creased or star filter is better, and in any case a hot solution filters more rapidly. Precipitates must be thoroughly washed, though only the first part of the wash water should be saved with the filtrate. If the precipitate is granular and settles readily, it may be advantageously washed by decantation before it is collected on a filter. A precipitate may be removed from the filter with a small spatula, or by washing it off with a stream of water, and removing by decantation most of the water. A precipitate may be readily dried by supporting the filter over a hot sand-bath, either in the funnel or on a triangle.

In fusions the well-dried substances should be intimately mixed in a mortar ; the crucible containing the mixture should be supported just

above the point of the blue cone of the lamp flame. The removal of the fused mass from a platinum crucible is much facilitated by setting it, while cooling, upon a thick, cold bit of metal.

In blowpipe work full time must be allowed for reduction on charcoal. With borax but little substance must be used, and care must be taken to get a good oxidizing or reducing flame, as the case may be.

It is essential that concise and accurate notes should be kept of all laboratory work. They should record the reactions, the conditions under which they take place, and the conclusions drawn from them. In other words, they should give in order what is done, what is observed, and what is inferred. These notes should be taken as the work is done, and are of value only as they are a truthful record of fact.



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# QUALITATIVE ANALYSIS.

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## BASES.

### GROUP I

Sulphides and carbonates soluble :

Na, K, Li,  $H_4N$ , *Cs*, *Rb*.

### GROUP II

Sulphides soluble, carbonates insoluble :

Ba, Sr, Ca, Mg.

### GROUP III

Sulphides not formed in wet way.  $(H_4N)_2S + Aq$  precipitates hydrates :

$Al$ ,  $Cr$ , *Th*, *Zr*, *G*, *Y*, *E*, *Ce*, *La*, *D*, *Cb*, *Ta*.

### GROUP IV.

Sulphides not formed in acid solutions, but precipitated in alkaline :

Fe,  $Fe^*$ , Ni, Co, Mn, Zn, *U*, *V*, *Te*, *In*.

### GROUP V.

Sulphides formed in acid solutions, insoluble in alkaline :

Ag, Hg,  $Hg_2$ , Pb, Cu, Cd, Bi, *Rh*, *Os*, *Ru*, *Pd*.

### GROUP VI

Sulphides formed in acid solutions, soluble in alkaline :

As, Sb, Sn,  $Sn^{IV}$ , *Au*, *Pt*, *Ir*, *W*, *Mo*, *Te*, *Se*.

\* Is precipitated as Fe S.

## PROPERTIES OF BASES.

## GROUP I Na, K, Li, H.N.

**Metals.**—Na, K, Li. Soft, very fusible, and lighter than water. Oxidize rapidly in air, or in water setting free  $H_2$ .  $H_4N$ . Known only in combination, as it is decomposed, when set free, into  $2NH_3$  and  $H_2$ .

**Oxides.**— $Na_2O$  and  $K_2O$  absorb water eagerly from the air,  $Li_2O$  unites with water readily,  $(H_4N)_2O$  unknown.

**Hydrates.**— $NaOH$  and  $KOH$  are deliquescent,  $LiOH$  sparingly soluble, and  $H_4NOH$  known only in solution.

**Sulphides.**—All soluble.

**Chlorides.**— $LiCl$  is deliquescent, the rest readily soluble.  $K_2PtCl_6$  and  $(H_4N)_2PtCl_6$  are quite insoluble in water, or  $HCl + Aq$ , more insoluble in alcohol. The other double chlorides with Pt are soluble.

**Carbonates.**— $Li_2CO_3$  sparingly soluble, the other neutral carbonates readily soluble,  $K_2CO_3$  deliquescent.

$KHCO_3$  and  $NaHCO_3$  are less soluble than the neutral salts,  $LiHCO_3$  more soluble.

**Sulphates.**— $Na_2SO_4$ ,  $(H_4N)_2SO_4$  and  $Li_2SO_4$  very soluble,  $K_2SO_4$  less so. The acid salts of the form  $MHSO_4$  are all more soluble than the neutral.

**Chromates.**—All soluble. The salts of the form  $M_2CrO_4$  give a yellow solution, of the form  $M_2Cr_2O_7$  a red.

**Phosphates.**—All Na, K and  $H_4N$  salts soluble.  $Na_2HPO_4 + Aq$  precipitates  $Li_3PO_4$  insoluble in water, quite soluble in  $H_4NCl + Aq$ , and soluble in acids.

**Oxalates.**—All soluble,  $KHC_2O_4$  not readily.

**Tartrates.**—Salts of the form  $M_2C_4H_4O_6$ , all soluble.  $KHC_4H_4O_6$  and  $H_4NHC_4H_4O_6$  are sparingly soluble in cold water.  $HC_4H_4O_6$  does not increase the solubility, though they are soluble in mineral acids, or in an alkaline solution. The other acid salts readily soluble.

**Cyanides.**—Soluble in water, the salts readily decomposed in solution.

**Ferrocyanides.**—All soluble.

## GROUP II. Ba, Sr, Ca, Mg.

**Metals.**—Harder than metals of Gr. I. Ba, Sr, and Ca oxidize rapidly in air or water, Mg slowly in moist air, or water at  $100^\circ$ .

**Oxides.**—Combine with water to form hydrates.

**Hydrates.**— $BaO \cdot H_2O$  is soluble,  $SrO \cdot H_2O$  less so;  $CaO \cdot H_2O$  sparingly soluble, and the solubility decreased by heat.  $MgO \cdot H_2O$  is insoluble in water, though soluble in solutions of  $H_4N$  salts. All are readily soluble in acids.  $NaOH + Aq$  precipitates the hydrates of the group; Ba, Sr and Ca hydrates only from concentrated solutions.  $H_4NOH + Aq$  precipitates only  $MgO \cdot H_2O$ , that partially, or not at all, in presence of  $H_4NCl$ .

**Sulphides.**— $BaS$ ,  $SrS$  and  $CaS$  are soluble;  $MgS$  decomposes water, and therefore is not formed in the wet way.

**Chlorides.**— $BaCl_2$  and  $SrCl_2$  readily soluble,  $CaCl_2$  and  $MgCl_2$  deliquescent.  $MgCl_2$  in solution is partially decomposed by evaporation to dryness.

**Carbonates.**—Carbonates of the form  $M''CO_3$ , insoluble in water, soluble in acids.  $CaCO_3$  and  $SrCO_3$  are



slightly soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ ,  $\text{BaCO}_3$  more markedly  $\text{MgCO}_3$  readily.  $\text{Na}_2\text{CO}_3 + \text{Aq}$  precipitates Ba, Sr and Ca as carbonates, Mg as basic carbonate.  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$  precipitates Ba, Sr and Ca completely, Mg partially in concentrated solutions, or not at all in presence of  $\text{H}_4\text{NCl}$ . The salts of the form  $\text{M}''\text{H}_2(\text{CO}_3)_2$  are soluble; on boiling their solutions the neutral carbonates are precipitated.

**Sulphates.**— $\text{BaSO}_4$  and  $\text{SrSO}_4$  are insoluble,  $\text{CaSO}_4$  sparingly soluble in cold water, less in hot,  $\text{MgSO}_4$  readily soluble. Mineral acids increase the solubility of  $\text{BaSO}_4$  but slightly, of  $\text{SrSO}_4$  and  $\text{CaSO}_4$  very decidedly. In strong  $\text{H}_2\text{SO}_4$  all these are soluble, forming acid salts  $\text{M}''\text{H}_2(\text{SO}_4)_2$ , decomposed by water with formation of  $\text{M}''\text{SO}_4$ .

**Chromates.**— $\text{BaCrO}_4$  insoluble in water or  $\text{HC}_2\text{H}_3\text{O}_2$ , soluble in  $\text{HCl} + \text{Aq}$  or  $\text{HNO}_3$ .  $\text{SrCrO}_4$  quite soluble in water, readily in  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{CaCrO}_4$  and  $\text{MgCrO}_4$  soluble in water.

**Phosphates.**—Of the three classes of phosphates, those of the form  $\text{M}''_2(\text{PO}_4)_3$  are insoluble; those of the form  $\text{M}''_3\text{H}_2(\text{PO}_4)_4$  are practically insoluble in water, though the Ba and Sr salts are markedly soluble and the Ca salt somewhat soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ . The salts of the form  $\text{M}''\text{H}_2(\text{PO}_4)_2$  are soluble in water. The insoluble salts are soluble in acids. In neutral solution  $\text{Na}_2\text{HPO}_4 + \text{Aq}$  precipitates phosphates of the form  $\text{M}''_2\text{H}_2(\text{PO}_4)_4$  in an  $\text{H}_4\text{NOH}$  solution Ba, Sr and Ca precipitated in the form  $\text{M}''_2(\text{PO}_4)_3$ . Mg is precipitated by  $\text{Na}_2\text{HPO}_4 + \text{Aq}$  in presence of  $\text{H}_4\text{NCl}$  and  $\text{H}_4\text{NOH}$  as  $\text{Mg}_3(\text{H}_4\text{N})_2(\text{PO}_4)_4$ , insoluble in water, though soluble in acids.

**Oxalates.**—Neutral oxalates of the form  $\text{M}''\text{C}_2\text{O}_4$  in-

soluble in water, soluble in mineral acids;  $\text{MgC}_2\text{O}_4$  is soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ .

**Tartrates.**—Neutral salts of Ba, Sr and Ca insoluble in water, soluble in mineral acids, or  $\text{NaOH} + \text{Aq}$ ; more or less soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ .  $\text{MgC}_2\text{H}_4\text{O}_4$  sparingly soluble in water, readily soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ .

**Cyanides.**—Soluble in water, the solutions decomposed by heat.

**Ferrocyanides.**— $\text{Ba}_4\text{Fe}(\text{CN})_6$  sparingly soluble, the rest soluble.

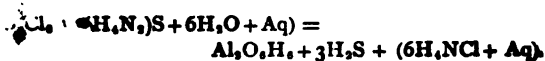
### GROUP III. Al, Cr.

**Metals.**—Al white, ductile, fusible, and does not readily oxidize. It is soluble in  $\text{HCl} + \text{Aq}$ , in dilute  $\text{H}_2\text{SO}_4$ , or in  $\text{NaOH}$ , + Aq with difficulty in  $\text{HNO}_3$ . Cr very hard and infusible.

**Oxides.**—Insoluble in water; before ignition they are soluble in acids, after ignition insoluble. Fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  converts  $\text{Al}_2\text{O}_3$  into soluble  $\text{Na}_2\text{O}_2\text{Al}_2$  and  $\text{Cr}_2\text{O}_3$  into  $\text{Na}_2\text{CrO}_4$ .

**Hydrates.**—Insoluble in water, soluble in acids, or  $\text{NaOH} + \text{Aq}$ . Cr, precipitated from  $\text{NaOH}$  solution by boiling as  $\text{Cr}_2\text{O}_3\text{H}_2$ , Al, is not. Both slightly soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ , the solubility of  $\text{Al}_2\text{O}_3\text{H}_2$  diminished by presence of  $\text{H}_4\text{NCl}$ . On heating the solution the dissolved hydrates are precipitated.

**Sulphides.**—Not formed in the wet way  $\text{Al}_2\text{S}_3$  decomposes water, liberating  $\text{H}_2\text{S}$  and forming  $\text{Al}_2\text{O}_3\text{H}_2$ .  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  precipitates  $\text{Al}_2\text{O}_3\text{H}_2$  and  $\text{Cr}_2\text{O}_3\text{H}_2$  with evolution of  $\text{H}_2\text{S}$ .<sup>1</sup>



**Chlorides.**—Soluble,  $\text{Al}_2\text{Cl}_6$  deliquescent.

**Carbonates.**—Normal salts unknown.  $\text{Na}_2\text{CO}_3 + \text{Aq}$  or  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$  precipitate essentially  $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$  and  $\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}$  with escape of  $\text{CO}_2$ .<sup>1</sup>

**Sulphates.**—Soluble. Most commonly found with  $\text{K}_2\text{SO}_4$  as alums.

**Phosphates.**—Salts of the form  $(\text{M}_3)^{\text{VI}}\text{H}_{18}(\text{PO}_4)_6$  are soluble, the other phosphates insoluble in water, soluble in acids or  $\text{NaOH} + \text{Aq}$ ; the Cr, salts precipitated on boiling the  $\text{NaOH}$  solution.

**Oxalates.**—The normal Al, salt insoluble, the Cr, salt soluble.

**Tartrates.**—Readily soluble in water. From their solutions  $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$  and  $\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}$  cannot be precipitated.

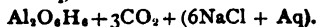
**Cyanides.**— $\text{Cr}_2(\text{CN})_6$  insoluble in water, slowly soluble in  $\text{KCN} + \text{Aq}$ .

#### GROUP IV. Fe, Ni, Co, Mn, Zn.

**Metals.**—Fe, Ni, Co, Mn, hard, fuse only at high temperatures, Zn soft, readily fusible, boils at red heat. Mn and Fe oxidize readily in moist air, Co and Ni do not. All soluble in acids.

**Oxides.**—All insoluble in water, soluble in acids, though  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  dissolve very slowly after ignition.  $\text{MnO}_2$  dissolves in  $\text{HCl} + \text{Ag}$  with evolution of  $\text{Cl}_2$ .<sup>2</sup>

**Hydrates.**—Insoluble in water, soluble in acids.  $\text{FeO}_2\cdot\text{H}_2\text{O}$ , white, rapidly turning green or black, and  $\text{MnO}_2\cdot\text{H}_2\text{O}$ .



<sup>2</sup>  $(\text{MnO}_2 + 4\text{HCl} + \text{Aq}) = (\text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Aq})$ . The solution then gently heated;  $(\text{MnCl}_2 + \text{Aq}) = (\text{MnCl}_2 + \text{Aq}) + \text{Cl}_2$ .

flesh colored, turning brown, are soluble in  $H_4NCl + Aq$ ;  $NiO, H_2O$ , pale green, and  $CoO, H_2O$ , pink, are soluble in  $H_4NOH + Aq$  or  $H_4NCl + Aq$ ;  $ZnO, H_2O$ , white, is soluble in  $H_4NOH + Aq$ ,  $NaOH + Aq$  or  $H_4NCl + Aq$ .  $H_4NOH + Aq$  and  $NaOH + Aq$  precipitate the hydrates, —with Co a blue basic salt in the cold, but the hydrate on boiling.  $Mn_2O_3, H_2O$ , brown,  $Ni_2O_3, H_2O$ , black,  $Co_2O_3, H_2O$ , black, and  $Fe_2O_3, H_2O$ , red brown, are insoluble in water or  $H_4NCl + Aq$ , but soluble in acids.

**Sulphides.**—Insoluble in water or in solutions of the hydrates or sulphides of Gr. I. When moist they are oxidized upon exposure to the air, some of them, at least, turning into soluble sulphates.  $FeS$ , black,  $MnS$ , flesh colored, soluble in dilute acids;  $ZnS$ , ~~white, soluble in dilute~~ mineral acids, insoluble in  $HC_2H_3O_2$ ;  $NiS$ , black,  $CoS$ , black, insoluble in cold dilute acid, soluble in strong hot  $HCl + Aq$  or  $HNO_3$ . The sulphides are not precipitated by  $H_2S$  from acid, or, at best, partially from neutral solutions, except  $ZnS$ , which is precipitated from solution in  $HC_2H_3O_2$ .  $Fe_2S_3$  cannot be formed in the wet way. From solutions of  $Fe$ , salts  $(H_4N)_2S + Aq$  precipitates  $FeS$  with separation of  $S$ .<sup>1</sup> In acid solutions  $H_2S$  converts  $Fe$ , salts into  $Fe$ .<sup>2</sup>  $(H_4N)_2S + Aq$  precipitates the other members as hydrated sulphides.

**Chlorides.**—All readily soluble,  $ZnCl$ , very deliquescent.

**Carbonates.**—Neutral salts  $M''CO_3$ , insoluble in water, soluble in acids.  $FeCO_3$ , soluble,  $MnCO_3$ , slightly soluble in  $H_4NCl + Aq$ ;  $NiCO_3$ , and  $CoCO_3$ , are soluble in

<sup>1</sup>  $(Fe, Cl)_2 + 3 (H_4N)_2S + Aq = 2FeS + S + (6H_4NCl + Aq)$ .

<sup>2</sup>  $(Fe, Cl)_2 + H_2S + Aq = S + (2FeCl_2 + 2HCl + Aq)$ .

$\text{H}_4\text{NCl} + \text{Aq}$  or  $\text{H}_4\text{NOH} + \text{Aq}$ ;  $\text{ZnCO}_3$  soluble in  $\text{NaOH} + \text{Aq}$ ,  $\text{H}_4\text{NCl} + \text{Aq}$  or  $\text{H}_4\text{NOH} + \text{Aq}$ . From solutions of Fe, salts soluble carbonates precipitate essentially  $\text{Fe}_2\text{O}_3\text{H}_2$  with evolution of  $\text{CO}_2$ . From solutions containing other members of the group  $\text{Na}_2\text{CO}_3 + \text{Aq}$  precipitates basic carbonates;  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$  precipitates similar basic salts, those of Ni, Co and Zn being soluble in an excess.

**Sulphates.**—All readily soluble.

**Phosphates.**—Salts of the form  $\text{M}''\text{H}_2(\text{PO}_4)_2$  soluble, of the forms  $\text{M}''\text{H}_2(\text{PO}_4)_2$  and  $\text{M}''_2(\text{PO}_4)_3$  insoluble in water, soluble in acids, more or less soluble in solutions of the soluble salts of the same member of the group. The Mn salts are soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ ; the Ni and Co salts in  $\text{H}_4\text{NCl} + \text{Aq}$  or  $\text{H}_4\text{NOH} + \text{Aq}$ ; the Zn salts in  $\text{H}_4\text{NCl} + \text{Aq}$ ,  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{NaOH} + \text{Aq}$ .  $\text{Na}_2\text{HPO}_4 + \text{Aq}$  added in excess precipitates members of the group in the form  $\text{M}_3(\text{PO}_4)_2$ .

**Oxalates.**—The neutral salts insoluble in water, soluble in acids. The Ni and Co salts readily soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ ;  $\text{ZnC}_2\text{O}_4$  soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ ,  $\text{H}_4\text{NCl} + \text{Aq}$  and  $\text{NaOH} + \text{Aq}$ .

**Tartrates.**— $\text{ZnC}_2\text{H}_2\text{O}_4$  and  $\text{NiC}_2\text{H}_2\text{O}_4$  insoluble in water, soluble in acids or  $\text{NaOH} + \text{Aq}$ ;  $\text{MnC}_2\text{H}_2\text{O}_4$  and  $\text{FeC}_2\text{H}_2\text{O}_4$  sparingly soluble in water, readily soluble in  $\text{NaOH} + \text{Aq}$ ;  $\text{CoC}_2\text{H}_2\text{O}_4$  and  $\text{Fe}_2(\text{C}_2\text{H}_2\text{O}_4)_3$  soluble in water, the solutions not precipitated by  $\text{NaOH} + \text{Aq}$ , or  $\text{Na}_2\text{CO}_3 + \text{Aq}$ .

**Cyanides.**—With the exception of the Fe, salt, which is unknown, the cyanides are all insoluble in water and soluble in  $\text{KCN} + \text{Aq}$ .  $\text{Ni}(\text{CN})_2$  and  $\text{Co}(\text{CN})_2$  are also

soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ ,  $\text{Zn}(\text{CN})_2$  in  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{NaOH} + \text{Aq}$ . From the solutions in  $\text{KCN} + \text{Aq}$   $\text{Ni}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$  are reprecipitated by neutralizing the  $\text{KCN}$  with acids. The solutions of the other cyanides in  $\text{KCN} + \text{Aq}$  contain (in the case of  $\text{Mn}$  and  $\text{Co}$  only after heating or exposure to air)  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Mn}(\text{CN})_6$ , and  $\text{K}_4\text{Co}(\text{CN})_6$ , from which acids do not separate the simple cyanides, and from which  $\text{Fe}$ ,  $\text{Mn}$  and  $\text{Co}$  cannot be precipitated by ordinary reagents.

**Ferrocyanides.**—Insoluble in water, decomposed by  $\text{NaOH} + \text{Aq}$  into hydrate of the metal, and  $\text{Na}_4\text{Fe}(\text{CN})_6$ .  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , white,  $\text{Ni}_2\text{Fe}(\text{CN})_6$ , greenish white,  $\text{Co}_2\text{Fe}(\text{CN})_6$ , green,  $\text{FeK}_4\text{Fe}(\text{CN})_6$ , white, rapidly turning blue, and  $(\text{Fe}_2)_3(\text{Fe}(\text{CN})_6)_3$ , blue, insoluble in  $\text{HCl} + \text{Aq}$ ;  $\text{Mn}_2\text{Fe}(\text{CN})_6$ , reddish white, soluble in  $\text{HCl} + \text{Aq}$ . All are decomposed by heating with  $\text{H}_2\text{SO}_4$  diluted with  $\frac{1}{3}$  its volume of water;  $\text{HCN}$  evolved, and sulphates left.

#### GROUP V. Ag, Hg, Pb, Cu, Cd, Bi.

**Metals.**—Bi brittle, Ag and Pb soft, Cu and Cd harder, Hg liquid at ordinary temperatures. Exposed to the air Ag, Bi and Hg do not oxidize, Pb, Cu and Cd not readily. All but Ag oxidize rapidly at high temperatures.  $\text{HNO}_3$  is the best solvent for all, though Cd dissolves in any acid.  $\text{HCl} + \text{Aq}$  does not act upon Ag, Hg, Pb, or Bi, and acts upon Cu only in presence of O. Hot concentrated  $\text{H}_2\text{SO}_4$  dissolves all but Pb, which it affects but little.

**Oxides.**— $\text{Ag}_2\text{O}$ , brown, slightly soluble in water, readily soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ , and in solutions of chlorides, cyanides or hyposulphites or in  $\text{HNO}_3$ .  $\text{HgO}$ , yellow

or red, and  $\text{Hg}_2\text{O}$ , black, insoluble in water, soluble in  $\text{HNO}_3$ .  $\text{PbO}$ , reddish yellow,  $\text{CuO}$ , black,  $\text{Cu}_2\text{O}$ , red,  $\text{CdO}$ , brown, and  $\text{Bi}_2\text{O}_3$ , yellow, in solubility are like the hydrates.

**Hydrates.**—Ag and Hg form no hydrates.  $\text{PbO}_2\cdot\text{H}_2\text{O}$  is practically insoluble in water, though alkaline to test paper, readily soluble in  $\text{NaOH} + \text{Aq}$ .  $\text{CuO}_2\cdot\text{H}_2\text{O}$ , blue, and  $\text{Cu}_2\text{O}_2\cdot\text{H}_2\text{O}$ , orange yellow, insoluble in water, slightly soluble in cold  $\text{NaOH} + \text{Aq}$ , soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ , or in  $\text{H}_4\text{NOH} + \text{Aq}$ . On boiling  $\text{CuO}_2\cdot\text{H}_2\text{O}$  with  $\text{NaOH} + \text{Aq}$  it is converted into  $\text{CuO}$ , the small amount dissolved in the cold being precipitated;  $\text{CdO}_2\cdot\text{H}_2\text{O}$ , white, insoluble in water, soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ ;  $\text{BiO}_2\cdot\text{H}_2\text{O}$ , white, insoluble in water or  $\text{H}_4\text{NOH} + \text{Aq}$ . All these hydrates readily soluble in acids.

From solutions containing members of the group  
 7  $\text{NaOH} + \text{Aq}$  precipitates Ag,  $\text{Hg}_2$  and  $\text{Hg}$ , as oxides, the rest as hydrates,  $\text{PbO}_2\cdot\text{H}_2\text{O}$ , soluble in an excess;  $\text{H}_4\text{NOH} + \text{Aq}$  precipitates Ag as oxide,  $\text{Hg}$  and  $\text{Hg}_2$  as insoluble amine compounds, the rest as basic salts, or hydrates, the Ag, Cu, and Cd precipitates being soluble in an excess.

**Sulphides.**—Insoluble in water, cold dilute acids or solutions of the hydrates or sulphides of Gr. I.; all except  $\text{HgS}$  and  $\text{Hg}_2\text{S}$  soluble in hot dilute  $\text{HNO}_3$ .  $\text{HgS}$ , black,  $\text{Ag}_2\text{S}$ , black,  $\text{CuS}$ , black, and  $\text{Bi}_2\text{S}_3$ , black, may be completely precipitated from solutions containing  $\text{HCl} + \text{Aq}$ , unless present in very great excess.  $\text{PbS}$ , black, and  $\text{CdS}$ , yellow, are not completely precipitated, if much  $\text{HCl} + \text{Aq}$  is present. Hg solutions are precipitated by  $\text{H}_2\text{S}$  first white, then yellow, the color changing to brown red, and

becoming black only with excess of  $H_2S$ . The change of color is due to the formation of various insoluble compounds of  $HgS$  with undecomposed  $Hg$  salt.

**Chlorides.**— $AgCl$  insoluble in water or acids, soluble in  $H_4NOH + Aq$  and in solutions of chlorides, cyanides or hyposulphites.  $Hg_2Cl_2$  insoluble in water but gradually decomposed by boiling with water,  $HCl + Aq$  or solutions of chlorides;  $H_4NOH + Aq$  converts it into  $(Hg_2)_3H_4N_3Cl_3$ , black, insoluble in water or  $H_4NOH + Aq$ .  $PbCl_2$ , crystalline, sparingly soluble in cold water, still less soluble in dilute  $HCl + Aq$ , soluble in hot water, in concentrated  $HCl + Aq$ , or in  $NaOH + Aq$ .  $BiCl_3$  is soluble in a small quantity of water, more water separates  $BiOCl$ , white, insoluble in water, soluble in acids.  $HgCl_2$  and  $CuCl_2$  soluble in water,  $CdCl_2$  deliquescent.

**Carbonates.**—Neutral salts insoluble in water, soluble in acids.  $Ag_2CO_3$  and  $CuCO_3$  are readily soluble in  $H_4NOH + Aq$ ,  $PbCO_3$  soluble in  $NaOH + Aq$ . From solutions containing members of the group  $Na_2CO_3 + Aq$  precipitates carbonates, generally basic, insoluble in an excess;  $(H_4N)_2CO_3 + Aq$  precipitates  $Hg$  and  $Hg_2$ , as insoluble amine compounds, the rest as carbonates or basic salts, the  $Ag$  and  $Cu$  salts being readily soluble in an excess.

**Sulphates.**— $CuSO_4$  and  $CdSO_4$  readily soluble;  $HgSO_4$  and  $Bi_2(SO_4)_3$  decomposed by water, giving insoluble  $Hg_2SO_4$ , yellow, and  $Bi_2H_4SO_4$ , white;  $Ag_2SO_4$  sparingly soluble;  $PbSO_4$  insoluble in water, much more soluble in strong acids, readily soluble in  $NaOH + Aq$ , or in solutions of some  $H_4N$  salts, especially  $H_4NC_2H_5O$ , and  $(H_4N)_3C_4H_9O_6$ .



**Phosphates.**—The salts of the forms  $M''_2H_2(PO_4)$  and  $M''_3(PO_4)_2$  are insoluble in water, soluble in  $HNO_3$ , many of them in  $H_2NCl + Aq$ .  $Ag_3PO_4$  and the Cu salts are soluble in  $H_2NOH + Aq$ , the Pb salts in  $NaOH + Aq$ . From solutions of the members of the group  $Na_2HPO_4 + Aq$  precipitates Ag as  $Ag_3PO_4$  and, if added in excess, the rest in the form  $M''_3(PO_4)_2$ .

**Oxalates.**—Insoluble in water, soluble in  $HNO_3$ ,  $Ag_2C_2O_4$  and  $Cu_2C_2O_4$  soluble in  $H_2NOH + Aq$ ;  $PbC_2O_4$  soluble in  $NaOH + Aq$ .

**Chromates.**— $Ag_2CrO_4$  brick red, insoluble in water, soluble in  $H_2NOH + Aq$ , or  $HNO_3$ ;  $Hg_2CrO_4$  red, and  $Bi_2(CrO_4)_3$  yellow, insoluble in water, soluble in  $HNO_3$ ;  $PbCrO_4$  bright yellow, insoluble in water or  $HC_2H_3O_2$ , soluble in  $NaOH + Aq$ , with difficulty in  $HNO_3$ .  $CuCrO_4$  brown, soluble, and  $HgCrO_4$  sparingly soluble in water.

**Tartrates.**—The Cu, Cd and Hg salts sparingly soluble in water, the rest insoluble.  $Cu_2C_4H_4O_6$  is readily soluble in  $NaOH + Aq$ ;  $PbC_4H_4O_6$  soluble in  $H_2C_4H_4O_6 + Aq$  or in  $NaOH + Aq$ .

**Cyanides.**— $Hg(CN)_2$  soluble in water, the rest insoluble in water, soluble in  $HNO_3$ , except  $AgCN$ . In  $KCN + Aq$   $AgCN$ ,  $Cu(CN)_2$ ,  $Cd(CN)_2$  are soluble,  $Pb(CN)_2$  and  $Bi(CN)_3$  insoluble.  $KCN + Aq$  added to solutions of Hg salts precipitates Hg, forming  $Hg(CN)_2$  in solution.

**Ferrocyanides.**— $Pb_2Fe(CN)_6$  and  $Cd_2Fe(CN)_6$  insoluble in water, soluble in  $HNO_3$ ;  $Ag_2Fe(CN)_6$  white,  $Cu_2Fe(CN)_6$  red brown,  $Bi_2(Fe(CN)_6)_3$  white, insoluble in acids, or  $H_2NOH + Aq$ .

**GROUP VI As, Sb, Sn.**

**Metals.**—As and Sb brittle, Sn soft and malleable. As volatilizes without fusion ; Sb and Sn fuse readily. As oxidizes at ordinary temperatures, all oxidize readily when heated. As and Sb are hardly attacked by HCl + Aq, Sn is easily dissolved. HNO<sub>3</sub> oxidizes all three, Sn and Sb without solution. HCl + Aq with HNO<sub>3</sub> dissolve all.

**Oxides.**—As<sub>2</sub>O<sub>3</sub>, sparingly soluble, Sb<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>4</sub>, slightly soluble in water ; the rest insoluble in water. All soluble in HCl + Aq or HCl + Aq with HNO<sub>3</sub>. As<sub>2</sub>O<sub>3</sub> readily soluble in NaOH + Aq. SnO<sub>2</sub> is often insoluble in HCl + Aq, but rendered soluble by fusion with NaOH. SnO and Sb<sub>2</sub>O<sub>3</sub>, heated in air give SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>4</sub>. As<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>, when heated become As<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>5</sub>.

**Hydrates.**—H<sub>3</sub>AsO<sub>4</sub> known only in solution or in its salts, H<sub>3</sub>AsO<sub>4</sub> soluble. HSbO<sub>3</sub>, slightly soluble in water. The other hydrates are insoluble in water, soluble in HCl + Aq or NaOH + Aq. The Sn<sup>IV</sup> hydrates more readily soluble in KOH + Aq than in NaOH + Aq ; one modification of it insoluble in acids, and with great difficulty soluble in KOH + Aq.

**Sulphides.**—Insoluble in water or dilute acids, readily soluble in solutions of the hydrates or sulphides of Gr. I. If dissolved in soluble sulphides they form sulphur salts,<sup>1</sup> or if in solutions of the hydrates, a mixture of sulphur salt with oxygen salt.<sup>2</sup> On adding acid to either of the solutions the original sulphide is reprecipitated.

<sup>1</sup>  $As_2S_3 + (3(H,N)_2S + Aq) = (2(H,N)_2AsS_2 + Aq).$

<sup>2</sup>  $As_2S_3 + (6NaOH + Aq) =$

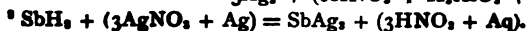
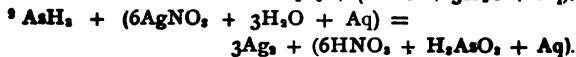
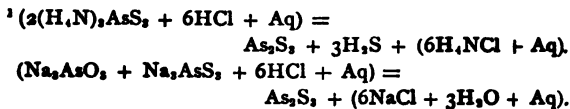
$(Na_2AsO_3 + Na_2AsS_2 + 3H_2O + Aq).$

tated.<sup>1</sup>  $\text{SnS}$  dissolved in yellow  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  precipitated as  $\text{SnS}_2$ .  $\text{As}_2\text{S}_3$ , yellow, insoluble in strong  $\text{HCl} + \text{Aq}$ , soluble in  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$ ;  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ , orange,  $\text{SnS}$ , brown,  $\text{SnS}_2$ , yellow, are soluble in strong  $\text{HCl} + \text{Aq}$ , insoluble in  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$ .  $\text{As}^{\text{v}}$  in acid solution is slowly reduced by  $\text{H}_2\text{S}$  and precipitated as  $\text{As}_2\text{S}_3$ .

**Chlorides.**— $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{SnCl}_4$ , volatile liquids;  $\text{SbCl}_3$ ,  $\text{SnCl}_4$ , solids. All decomposed by water;  $\text{SnCl}_4$  and  $\text{SnCl}_2$  slowly or when treated with a large amount.  $\text{SbCl}_3$  gives at once  $\text{SbOCl}$  insoluble in water, soluble in acids;  $\text{AsCl}_3$  gives  $\text{As}_2\text{O}_3$  as the chief product.

**Hydrides.**— $\text{AsH}_3$  and  $\text{SbH}_3$ , gaseous, are formed when a soluble As or Sb compound is treated with Zn and dilute  $\text{H}_2\text{SO}_4$ . They are decomposed below red heat into Sb or As and  $\text{H}_2$ . Passed into  $\text{AgNO}_3 + \text{Aq}$ ,  $\text{AsH}_3$  precipitates Ag and leaves  $\text{H}_3\text{AsO}_3$  in solution;<sup>2</sup>  $\text{SbH}_3$  precipitates  $\text{SbAg}_3$ .<sup>3</sup>

**Tartrates.**— $(\text{SbO})\text{KC}_4\text{H}_4\text{O}_6$ , soluble in water. The presence of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  in sufficient quantity prevents the precipitation of basic Sb salts by water.

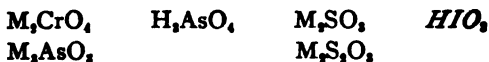


# ACIDS.

## GROUP I

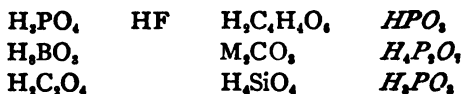
Ba Salts insoluble in water.

1. Acids decomposed in acid solution by  $H_2S$ .



2. Acids not decomposed in acid solution by  $H_2S$ .

- a. Ba Salts soluble in  $HCl + Aq$ .

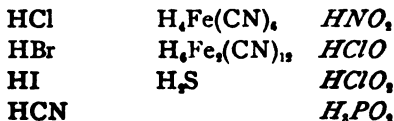


- b. Ba Salts insoluble in  $HCl + Aq$ .



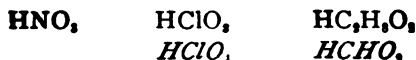
## GROUP II

Ba Salts soluble, Ag Salts insoluble in water.



## GROUP III

Ba and Ag Salts soluble in water.



## PROPERTIES OF ACIDS.

**GROUP I. 1.  $M_2CrO_4$ ,  $M_2AsO_4$ ,  $H_2AsO_4$ ,  $M_2SO_4$ ,  $M_2S_2O_4$ .**

**Chromates.**—Salts generally insoluble in water, the most important soluble salts being those of Gr. I., Sr, Ca, Mg, and the normal salts of Mn and Zn. The acid is unknown, since it breaks upon liberation from its salts into  $H_2O$  and  $CrO_3$ ; it also gives no salts of the form  $MHCrO_4$ . If acid be added to a solution of  $M_2CrO_4$  it turns from yellow to red with the formation of a salt of the form  $M_2Cr_2O_7$ ,<sup>1</sup> further addition of acid sets  $CrO_3$  free.<sup>2</sup> If  $H_2SO_4$  is used the  $CrO_3$  separates as a red mass, or in red needles.  $CrO_3$  heated with  $H_2SO_4$  loses oxygen and becomes  $Cr_2(SO_4)_3$ ,<sup>3</sup> with  $HCl + Aq$  it gives  $Cr_2Cl_6$ , water and  $Cl_2$ .<sup>4</sup> Organic matter or reducing agents, like  $H_2S$  or  $SO_2$ , effect a similar change,  $2CrO_3$  becoming  $Cr_2O_3$ .<sup>5</sup> In any case the change of  $CrO_3$  to  $Cr_2O_3$  is accompanied by a corresponding change of color from red to green.  $BaCrO_4$  and  $PbCrO_4$ , yellow, insoluble in water or in  $HCl, H_2O_2$ .  $Ag_2CrO_4$ , brick red, soluble in  $HNO_3$  or  $H_2NOH + Aq$ .

**Arsenites.**—The salts of Gr. I. are soluble, the neutral salts of the other groups insoluble in water, though many are soluble in  $H_4NCl + Aq$ . The acid is unknown,

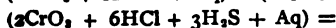
$$^1 (2M_2CrO_4 + H_2SO_4 + Aq) =$$



$$^2 (K_2Cr_2O_7 + H_2SO_4 + Aq) = (2CrO_3 + K_2SO_4 + H_2O + Aq)$$



$$^4 (2CrO_3 + 12HCl + Aq) = (Cr_2Cl_6 + 6H_2O + Aq + 3Cl_2).$$



although acid salts of the forms  $MH_2AsO_4$  and  $M_2HAsO_4$  are known. From acid solutions of all salts  $H_2S$  readily precipitates  $As_2S_3$  yellow. Oxidizing agents convert the salts into arseniates.  $Cu_3H_2(AsO_4)_2$  is green, insoluble in water, soluble in acids, and soluble in  $NaOH + Aq$ . On warming the  $NaOH$  solution  $Cu_2O \cdot H_2O$ , orange yellow, is precipitated,  $Na_2AsO_4$  being left in solution.  $Mg_3(AsO_4)_2$  and  $Ba_3(AsO_4)_2$ , insoluble in water, soluble in acids, or  $H_4NCl + Aq$ ;  $Ag_3AsO_4$ , pale yellow, insoluble in water, soluble in  $H_4NOH + Aq$  or  $HNO_3$ .

**Arseniates.**—The salts resemble the phosphates closely. Of the neutral salts only those of Gr. I. are soluble. The acid is solid, soluble in water. From acid solutions of its salts  $H_2S$  at first precipitates nothing, but on long standing, or more quickly on warming, it is reduced and  $As_2S_3$  is precipitated.  $SO_2$  reduces it quite rapidly to arsenious acid with formation of  $H_2SO_4$ ;  $H_2S$  then at once precipitates  $As_2S_3$ .  $Ba_3(AsO_4)_2$  and  $Mg_3(AsO_4)_2$  are insoluble in water, soluble in acids.  $Ag_3AsO_4$ , red brown, insoluble in water, soluble in  $H_4NOH + Aq$  or  $HNO_3$ .  $Mg_3(H_4N)_2(AsO_4)_2$ , insoluble in water or  $H_4NCl + Aq$ , soluble in acid, is formed when  $H_4NOH + Aq$ ,  $H_4NCl + Aq$  and  $MgSO_4 + Aq$  are added to aqueous solutions of arseniates. A solution of  $(H_4N)_2MO_4$  in  $HNO_3$  gives no precipitate in acid solutions of arseniates in the cold, but gives a yellow precipitate on boiling.

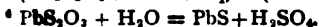
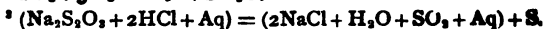
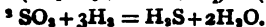
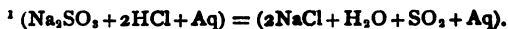
**Sulphites.**—The neutral salts are all insoluble or sparingly soluble in water; of the acid salts many are soluble, though many are decomposed by boiling their solutions, neutral salts being formed. The acid is un-

known. From its salts stronger acids liberate  $\text{SO}_2$ , soluble in water; in this solution  $\text{H}_2\text{S}$  forms  $\text{H}_2\text{S}_2\text{O}_3$  with separation of  $\text{S}$ .  $\text{SO}_2$  is a powerful reducing agent but is itself reduced by nascent  $\text{H}$  with formation of  $\text{H}_2\text{S}$ .<sup>1</sup>  $\text{BaSO}_3$  is insoluble in water, soluble in  $\text{HCl} + \text{Aq}$ ; from this solution  $\text{Cl}_2$  or  $\text{Br}_2$  precipitate  $\text{BaSO}_4$ .

**Hyposulphites.**—Most of the salts are soluble in water. The acid is unknown. Stronger acids liberate from its salts  $\text{SO}_2$  and  $\text{S}$ . The same decomposition<sup>2</sup> takes place when  $\text{HCl} + \text{Aq}$  is added to solutions of its salts, though slowly in dilute solutions. With  $\text{H}_2\text{S}$  in acid solutions, or with nascent hydrogen the reactions are the same as with the sulphites.  $\text{BaS}_2\text{O}_3$  insoluble in water soluble in  $\text{HCl} + \text{Aq}$ .  $\text{Ag}_2\text{S}_2\text{O}_3$ , white, insoluble in water, soluble in solutions of hyposulphites; blackens on heating,  $\text{Ag}_2\text{S}$  being formed.  $\text{PbS}_2\text{O}_3$ , insoluble in water, soluble in solutions of hyposulphites, forms  $\text{PbS}$  on heating.<sup>4</sup>

**GROUP I 2.** (a)  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HF}$ ,  $\text{M}_2\text{CO}_3$ ,  $\text{H}_2\text{SiO}_3$ ,  $\text{H}_2\text{C}_2\text{H}_3\text{O}_4$ ; (b)  $\text{H}_2\text{SO}_4$ .

**Phosphates.**—Salts of the forms  $\text{M}_3\text{PO}_4$  and  $\text{M}_2\text{HPO}_4$  insoluble except those of Gr. I., salts of the form  $\text{MH}_2\text{PO}_4$  soluble. All the insoluble salts are soluble in acids, and these solutions are precipitated by  $\text{H}_2\text{NOH} + \text{Aq}$ ; the precipitate is usually a phosphate of the form  $\text{M}_3\text{PO}_4$ .  $\text{Ba}_3(\text{PO}_4)_2$  and  $\text{Ca}_3(\text{PO}_4)_2$ , insoluble in water, are soluble in  $\text{HCl} + \text{Aq}$  and in  $\text{HC}_2\text{H}_3\text{O}_2$ .  $\text{Ag}_3\text{PO}_4$ , pale yellow, insoluble in water, is soluble in  $\text{H}_2\text{NOH} + \text{Aq}$  or



**HNO<sub>3</sub>.** From aqueous solutions of the phosphates  $\text{MgSO}_4 + \text{Aq}$ , after adding  $\text{H}_4\text{NCl} + \text{Aq}$  and  $\text{H}_4\text{NOH} + \text{Aq}$ , precipitates  $\text{Mg}_3(\text{H}_4\text{N})_2(\text{PO}_4)_2$ , insoluble in water or  $\text{H}_4\text{NCl} + \text{Aq}$ , soluble in acids. In acid solutions of the phosphates  $(\text{H}_4\text{N})_2\text{MO}_4$  dissolved in  $\text{HNO}_3$  gives a yellow precipitate in the cold, insoluble in water or in dilute acids, if  $(\text{H}_4\text{N})_2\text{MO}_4$  be in excess, readily soluble in excess of phosphate.

**Borates.**—Only the salts of Gr. I. are readily soluble in water, though many salts insoluble in water are soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ . The acid is separated from its salts by stronger acids; soluble in water, the solution turning turmeric paper red, best seen when the paper is dried at  $100^\circ$ . This red color is changed to greenish black when moistened with  $\text{Na}_2\text{CO}_3 + \text{Aq}$ .  $\text{H}_3\text{BO}_3$  partially volatilized by evaporation of its solution. Its alcoholic solution burns with a green flame. The Ba and Ca salts are insoluble in water, soluble in  $\text{HCl} + \text{Aq}$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ , or  $\text{H}_4\text{NCl} + \text{Aq}$ . The Mg salt readily soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ .

**Oxalates.**—Almost all the neutral salts, except those of Gr. I. are insoluble in water, soluble in acids.  $\text{H}_4\text{NOH}$  precipitates the acid solutions of many of the salts insoluble in water, those of Ba, Sr and Ca completely. All the salts are decomposed by ignition; the residue consists of carbonate, oxide or metal. The acid, readily soluble in water, is decomposed when heated by itself or with strong  $\text{H}_2\text{SO}_4$  into  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$ .<sup>1</sup> With the dry salts  $\text{H}_2\text{SO}_4$  gives the same reaction, first setting the acid free, then decomposing it. The acid or its salts warmed with

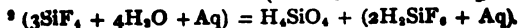
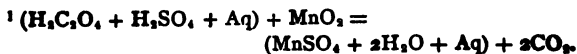
<sup>1</sup>  $\text{H}_2\text{C}_2\text{O}_4 = \text{H}_2\text{O} + \text{CO}_2 + \text{CO}$ .



dilute  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  give off  $\text{CO}_2$ ,  $\text{MnSO}_4$  and water being formed.<sup>1</sup>  $\text{BaC}_2\text{O}_4$  is insoluble in water, soluble in  $\text{HCl} + \text{Aq}$ .  $\text{CaC}_2\text{O}_4$  is insoluble in water or  $\text{HC}_2\text{H}_3\text{O}_2$ , soluble in  $\text{HCl} + \text{Aq}$ .  $\text{Ag}_2\text{C}_2\text{O}_4$  insoluble in water, soluble in  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{HNO}_3$ , is decomposed with explosion on ignition,  $\text{Ag}$  being left. The salts of Gr. II. are decomposed on boiling with a concentrated solution of  $\text{Na}_2\text{CO}_3$  with formation of the corresponding carbonates and  $\text{Na}_2\text{C}_2\text{O}_4$  in solution.

**Fluorides.**—Salts of Gr. I. readily soluble, as also  $\text{Al}_2\text{F}_6$ ,  $\text{Cr}_2\text{F}_6$ ,  $\text{Fe}_2\text{F}_6$ ,  $\text{AgF}$ ,  $\text{HgF}_2$ . The rest are sparingly soluble or insoluble in water.  $\text{HF}$  is liberated from its salts by strong  $\text{H}_2\text{SO}_4$  as a gas readily soluble in water, the solution characterized by its power of dissolving  $\text{SiO}_2$  or its compounds (glass). A fluoride mixed with silicates or  $\text{SiO}_2$  gives, on heating with strong  $\text{H}_2\text{SO}_4$ ,  $\text{SiF}_4$  fuming in the air, and giving with water  $\text{H}_4\text{SiO}_4$ , gelatinous.<sup>2</sup> Fluorides not decomposed by  $\text{H}_2\text{SO}_4$  must be fused with mixed  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .  $\text{BaF}_2$  and  $\text{CaF}_2$ , as precipitated, are gelatinous and transparent, soluble in hot  $\text{HCl} + \text{Aq}$ , though with difficulty, soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ .

**Tartrates.**—The neutral salts of Grs. I. and III. as well as of  $\text{Fe}$ , and  $\text{Co}$  readily soluble in water. The acid is very soluble in water, and its presence prevents partially or wholly precipitation with  $\text{NaOH} + \text{Aq}$ ,  $\text{H}_4\text{NOH} + \text{Aq}$ ,  $\text{Na}_2\text{CO}_3 + \text{Aq}$ , or  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$ . The acid and its salts char on heating, giving off an odor like



burnt sugar.  $\text{BaC}_4\text{H}_4\text{O}_6$  insoluble in water, soluble in  $\text{HCl} + \text{Aq}$  or  $\text{H}_4\text{NCl} + \text{Aq}$ .  $\text{CaC}_4\text{H}_4\text{O}_6$  insoluble in water, soluble in  $\text{HCl}$  or  $\text{HC}_2\text{H}_3\text{O}_2$ , quite soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ , readily soluble in cold  $\text{NaOH} + \text{Aq}$ , reprecipitated gelatinous on boiling;  $\text{Ag}_3\text{C}_4\text{H}_4\text{O}_6$ , white, insoluble in water, soluble in  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{HNO}_3$ ; blackens immediately on boiling from separated  $\text{Ag}$ .  $\text{KHC}_4\text{H}_4\text{O}_6$  is sparingly soluble in cold water,  $\text{HC}_2\text{H}_3\text{O}_2$ , or  $\text{H}_3\text{C}_4\text{H}_4\text{O}_6 + \text{Aq}$  readily soluble in mineral acids or solutions of hydrates of Gr. I.

**Carbonates.**—The neutral salts are all insoluble in water, except those of Gr. I.; the acid salts are generally soluble, though, if their solutions are boiled, all but those of Gr. I. are decomposed, and neutral salts precipitated. The acid is unknown, since it breaks up upon liberation from its salts into water and  $\text{CO}_2$ , a gas heavier than air, quite soluble in water.  $\text{CO}_2$  gives with  $\text{CaO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CaCO}_3$ , white.  $\text{BaCO}_3$  insoluble in water, soluble in acids.  $\text{Ag}_2\text{CO}_3$ , white, insoluble in water, soluble in  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{HNO}_3$ .

**Silicates.**—The silicates of Gr. I. are alone soluble in water; many of the insoluble salts are decomposed by strong acids with the separation of  $\text{H}_4\text{SiO}_4$ . When the acid is liberated from its salts by acids, the greater part generally separates in a gelatinous form, though more or less remains in solution. If such an acid solution is evaporated to dryness, all its Si is left as a hydrate, insoluble in water or acids (except  $\text{HFl} + \text{Aq}$ ).  $\text{H}_4\text{SiO}_4$  when once formed is insoluble in water or acids (except  $\text{HF} + \text{Aq}$ ), though soluble in  $\text{NaOH} + \text{Aq}$ , and reprecipitated from this solution by  $\text{H}_4\text{NCl} + \text{Aq}$ . It loses water readily,

and on ignition  $\text{SiO}_2$  is left insoluble in a bead of microcosmic salt ( $\text{NaH}_2\text{NPO}_4$ ). All silicates are decomposed by fusion with mixed  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . The Ba, Ca and Ag salts are insoluble, decomposed by  $\text{HCl} + \text{Aq}$ .

**Sulphates.**—The normal salts are all soluble, except  $\text{BaSO}_4$ ,  $\text{SrSO}_4$  and  $\text{PbSO}_4$ , insoluble. and  $\text{CaSO}_4$ , sparingly soluble. The acid has great affinity for water, and dissolves with evolution of heat. When strong it blackens organic water. Sulphates, when heated on charcoal with  $\text{Na}_2\text{CO}_3$  in the inner blowpipe flame, give  $\text{Na}_2\text{S}$ .  $\text{BaSO}_4$ , white, insoluble in water or acids.

**GROUP II**  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HCN}$ ,  $\text{H.Fe}_3(\text{CN})_6$ ,  
 $\text{H.Fe}_3(\text{CN})_{11}$ ,  $\text{H}_2\text{S}$ .

**Chlorides.**—All soluble except  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ , insoluble, and  $\text{PbCl}_2$ , sparingly soluble in water. From its salts  $\text{H}_2\text{SO}_4$  liberates  $\text{HCl}$  (with effervescence, if little or no water is present), a gas very soluble in water;  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  evolve  $\text{Cl}_2$ , a greenish gas, somewhat soluble in water, which bleaches.  $\text{AgCl}$  insoluble in water, or  $\text{HNO}_3$ , soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ .

**Bromides.**—Salts soluble except  $\text{AgBr}$  and  $\text{Hg}_2\text{Br}_2$ . From its salts  $\text{H}_2\text{SO}_4$  liberates  $\text{HBr}$ , a gas very soluble in water, but mixed with more or less  $\text{Br}_2$ ;  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  liberate  $\text{Br}_2$ , a red volatile liquid soluble in water, its vapors red. In solutions of the bromides  $\text{Cl}_2 + \text{Aq}$  liberates  $\text{Br}_2$ , which colors the liquid red. The  $\text{Br}_2$ , thus liberated, can all be collected in a little  $\text{CS}_2$ , in which it is much more soluble than in water. An excess of  $\text{Cl}_2$  bleaches the color.



**Iodides.**—Soluble except  $\text{AgI}$ , yellowish white,  $\text{Hg}_2\text{I}_2$ , greenish,  $\text{HgI}_2$ , red,  $\text{PbI}_2$ , yellow, and  $\text{Bi}_2\text{I}_6$ , insoluble in water. From its salts  $\text{H}_2\text{SO}_4$  liberates  $\text{HI}$ , but it is at once oxidized and  $\text{I}_2$  set free.  $\text{I}_2$  is almost insoluble in water, readily soluble in  $\text{CS}_2$ , which it colors violet; soluble, also, in solutions of iodides with a deep brown color. It sublimes with gentle heat, its vapor being violet.  $\text{Cl}_2$  liberates  $\text{I}_2$  from its salts, an excess of  $\text{Cl}_2$  then converts it into colorless  $\text{ICl}_3$ .  $\text{I}_2$  gives with dilute starch paste in a slightly acid solution a deep blue compound of starch and  $\text{I}_2$ , bleached by heat or  $\text{Cl}_2$ .  $\text{AgI}$  insoluble in water or  $\text{HNO}_3$ , scarcely soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ , soluble in solutions of iodides.

**Cyanides.**—Salts of Grs. I. and II. and  $\text{Hg}(\text{CN})_2$ , soluble, the rest insoluble in water though many are soluble in solutions of cyanides.  $\text{HCN}$  is a volatile liquid soluble in water. From the soluble salts even dilute acids liberate the acid; strong  $\text{H}_2\text{SO}_4$  decomposes it, giving  $\text{CO}$ . The insoluble salts are all decomposed by ignition. Many of the insoluble salts are decomposed by  $\text{HCl} + \text{Aq}$ , all by strong  $\text{H}_2\text{SO}_4$ .  $\text{AgCN}$ , white, insoluble in water or dilute  $\text{HNO}_3$ , soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ , or in solutions of cyanides of Grs. I. and II.

**Ferrocyanides.**—All insoluble in water except the salts of Grs. I. and II. Many of the salts are colored, and all the insoluble salts decomposed by  $\text{NaOH} + \text{Aq}$  or  $\text{H}_2\text{SO}_4$ .  $\text{H}_4\text{Fe}(\text{CN})_6$  is a white solid readily soluble in water.  $\text{Cl}_2$  converts  $\text{K}_4\text{Fe}(\text{CN})_6$  in solution into  $\text{K}_4\text{Fe}_2(\text{CN})_{12}$ .  $\text{Ag}_4\text{Fe}(\text{CN})_6$ , white, insoluble in water,  $\text{H}_4\text{NOH} + \text{Aq}$  or  $\text{HNO}_3$ .  $(\text{Fe}_3)_4(\text{Fe}(\text{CN})_6)_3$ , blue, and  $\text{Cu}_4\text{Fe}_2(\text{CN})_{12}$ , red brown, insoluble in water, or  $\text{HCl} + \text{Aq}$ .

**Ferriocyanides.**—Salts of Grs. I. and II. and  $\text{Fe}_3$  soluble in water. Many of the salts are colored, and all insoluble salts decomposed by  $\text{NaOH} + \text{Aq}$  or  $\text{H}_2\text{SO}_4$ . The acid,  $\text{H}_4\text{Fe}_2(\text{CN})_{12}$ , is readily soluble in water and converted by reducing agents into  $\text{H}_4\text{Fe}(\text{CN})_6$ .  $\text{Ag}_3\text{Fe}_3(\text{CN})_{12}$ , orange, insoluble in water, or  $\text{HNO}_3$ , soluble in  $\text{H}_4\text{NOH} + \text{Aq}$ .  $\text{Fe}_3\text{Fe}_3(\text{CN})_{12}$ , blue, insoluble in water, or  $\text{HCl} + \text{Aq}$ .  $\text{Fe}_2\text{Fe}_3(\text{CN})_{12}$ , soluble in water, the solution brown.

**Sulphides.**—The salts of Grs. I. and II. soluble, the rest insoluble in water. The salts of Gr. VI. soluble in  $\text{NaOH} + \text{Aq}$ . Most salts attacked by hot  $\text{HCl} + \text{Aq}$ , and all by  $\text{HCl} + \text{Aq}$  with  $\text{HNO}_3$ . Solution is effected by  $\text{HCl} + \text{Aq}$  with liberation of the acid  $\text{H}_2\text{S}$ , a gas somewhat soluble in water; by  $\text{HNO}_3$ , or  $\text{HCl} + \text{Aq}$  with  $\text{HNO}_3$ , with separation of S, which by boiling is slowly oxidized to  $\text{H}_2\text{SO}_4$ .  $\text{Ag}_2\text{S}$ , black, insoluble in  $\text{H}_4\text{NOH} + \text{Aq}$ , soluble in hot  $\text{HNO}_3$ .

### GROUP III. $\text{HNO}_3$ , $\text{HClO}_3$ , $\text{HC}$ , $\text{H}_2\text{O}_2$ .

**Nitrates.**—Normal salts all soluble in water. From its salts  $\text{H}_2\text{SO}_4$  liberates  $\text{HNO}_3$ , a fuming liquid, perfectly soluble in water. By the action of  $\text{HNO}_3$  upon Cu, NO is formed<sup>1</sup>, a colorless gas, which with the O of the air forms  $\text{NO}_2$ , orange red. NO is also soluble in a concentrated solution of  $\text{FeSO}_4$ , forming a solution colored black, brown, or reddish, according to its concentration. On heating the solution NO is set free. All the salts deflagrate when heated on charcoal, and all are decomposed by ignition.

**Chlorates.**—Normal salts all soluble in water.  $\text{H}_2\text{SO}_4$



added to the chlorates liberates  $\text{Cl}_2\text{O}_6$ , a yellow green gas, smelling like  $\text{Cl}_2$ , and bleaching, the  $\text{H}_2\text{SO}_4$  becoming yellow. Heat must be avoided or the decomposition is accompanied by explosion.  $\text{HCl} + \text{Aq}$  liberates a gas of similar color and odor,  $\text{Cl}_2\text{O}_3$ .  $\text{HClO}_2$  is liquid, easily decomposed, and readily soluble in water. All the salts deflagrate when heated on charcoal, and are decomposed on ignition into chloride and  $\text{O}_2$ .

**Acetates.**—The normal salts are all soluble in water, although many are decomposed by boiling their solutions into insoluble basic salts. The salts are all decomposed by ignition; acetone,  $\text{C}_2\text{H}_5\text{O}$ , is almost always one of the products of decomposition, and generally  $\text{HC}_2\text{H}_3\text{O}_2$ . Salts of Grs. I. and II. give a residue of carbonate, the rest either metal or oxide, generally mixed with C.  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_4$  gives a deep red solution, which on boiling deposits all the Fe, as a brown basic salt insoluble in water.

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## COURSE OF ANALYSIS.

### PRELIMINARY EXAMINATION.

The physical properties of the substance under examination must first be carefully noted. A solid must, if possible, be reduced to fine powder; a portion of a liquid should be evaporated to dryness, and the residue, if any is left, powdered. A small quantity only is needed for each test.

#### Heat in a Bulb Tube.

**Water is given off.**—Crystal water usually given off with fusion, water of constitution without; water mechanically enclosed often with decrepitation. If the

water has an alkaline reaction,  $H_4N$  is present; if an acid reaction, some volatile acid as  $H_2SO_4$ ,  $HCl$ ,  $HNO_3$ , etc.

**Gas escapes.**— $O_2$  shows presence of nitrates, chlorates, or dioxides; a glowing match kindles.

$CO_2$  shows presence of carbonates, or certain oxalates; a drop of  $CaO, H_2O + Aq$  rendered turbid.

$CO$  shows presence of  $H_2C_2O_4$  or some of its salts; burns with a blue flame.

$H_2S$  shows presence of hydrous sulphide; recognized by its odor.

$CN$  formed from cyanides decomposed by heat; recognized by odor, or burning with crimson flame.

$NO_2$  shows presence of nitrates; recognized by orange red color, and odor.

$Cl_2$ ,  $Br_2$ , or  $I_2$  liberated from chlorides, bromides or iodides which are decomposed by heat.

$H_4N$  usually shows the decomposition of an  $H_4N$  salt; recognized by test paper, and odor.

$SO_2$  often formed by decomposition of sulphates.

**Sublimate formed.**

$S$  sublimes from many sulphides in red brown drops; solidifies yellow on cooling.

$I_2$  from many iodine compounds; vapor violet, the sublimate black.

$H_4N$ . Most salts give white crystalline sublimes.

$Hg$  and some of its compounds.  $Hg$  white metallic globules;  $HgS$  black, turns red when rubbed;  $HgCl_2$  melts and sublimes white,  $Hg_2Cl_2$  sublimes without melting.  $HgI_2$ , red, sublimes yellow, turns red when rubbed.

$As$  and some of its compounds.  $As$  gives a metallic

mirror,  $\text{As}_2\text{O}_3$ , a crystalline sublimate;  $\text{As}_2\text{S}_3$  sublimes reddish yellow when hot, yellow when cold.

$\text{Sb}_2\text{O}_3$  melts and sublimes in needles.

$\text{H}_2\text{C}_2\text{O}_4$  sublimes in part, white and crystalline.

**Residue left with change of color.**—A black residue may be due to the formation of a black oxide, or to carbonization showing the presence of an organic acid or other organic matter. In the latter case a characteristic odor is usually evolved. If the residue effervesces with acids, while the original substance did not, it shows the presence of acetates, tartrates, or oxalates of Grs. I. and II. The following changes of color are common. The residue

Yellow	while hot	White	when cold	$\text{ZnO}$
Red brown	" "	Yellow	" "	$\text{PbO}$
Red brown	" "	Pale yellow	" "	$\text{Bi}_2\text{O}_3$
Black	" "	Red	" "	$\text{Fe}_2\text{O}_3$

**Heat on charcoal in inner blowpipe flame.**—Many of the reactions of the closed tube are repeated. If the odor of  $\text{SO}_2$  is perceived sulphides are probably present. A garlic odor shows presence of As.

**Deflagration.**—Shows presence of nitrates or chlorates.

**Substance melts** and runs into the charcoal. Salts of Gr. I.

**Residue white;** infusible, but luminous when heated, Gr. II., Zn, Al, or  $\text{SiO}_2$ . The residue must then be moistened with  $\text{Co}(\text{NO}_3)_2$ , + Aq and again heated in the outer flame. If the residue becomes colored, blue shows Al; green Zn; flesh colored, Mg; blue green, Sn. Phosphates and silicates also give a blue color.



**Residue colored or metallic**, with or without a coating upon the charcoal. In this case some of the substance must be mixed with  $\text{Na}_2\text{CO}_3$  and heated in the inner blowpipe flame on charcoal. The color of the coating around the assay, and the nature of the metallic globule must be noted. If no one large globule can be obtained, the charcoal under the assay must be cut out and ground up with water in a mortar. The charcoal can readily be washed away and the metal left, in spangles, if malleable. The presence of As shown by garlic odor. The character of the metallic globules of the reducible metals and the colors of the coating on the charcoal are as follows :

**ON CHARCOAL WITH  $\text{Na}_2\text{CO}_3$ .**

	GLOBULE.	COATING.	
		Hot.	Cold.
Bi	Brittle	Dark orange	Lemon yellow
Sb	"	White	White
Ag	Malleable	(Dark red)	
Sn	"	Pale yellow	White
Pb	"	Orange yellow	Yellow
Cu	"		
Zn		Yellow	White
Co		Red brown	Red brown
As			White
Co	} Reduced but not fused.		
Ni			
Fe			

**Examination with Borax.**

**A small quantity of the substance is melted into a**

borax bead upon platinum wire. It should first be heated in the outer blowpipe flame, afterwards in the inner flame, the colors of the bead, both hot and cold, being carefully noted. An excess of substance must be avoided. The colors of the various beads, both hot and cold, in the inner and outer flames, are as follows :

**BORAX BEADS.**

	OUTER FLAME.		INNER FLAME.	
	Hot.	Cold.	Hot.	Cold.
Cu	Green	Blue	Colorless	Red opaque
Co	Blue	Blue	Blue	Blue
Ni	Violet	Red brown	Gray	Gray
Fe	Red	Yellow	Bottle green	Bottle green
Mn	Violet	Amethyst	Colorless	Colorless
Cr	Green	Green	Green	Green

**Flame Colorations.**

The coloration given by the substance to the flame of the lamp often gives more or less positive indications. The substance is introduced into the edge of the flame on platinum wire.

Red flames. K, violet ; Li, carmine ; Sr, crimson ; Ca, orange red.

Yellow flames. Na.

Green flames. Cu (most salts) bright green ; Ba, yellow green ;  $H_2BO_3$ , pale green.

Blue flames.  $CuCl_2$ , bright blue ; Pb, As pale blue.

**Examination with  $H_2SO_4$ .**

On heating the substance with strong  $H_2SO_4$ , the

presence or absence of certain acids may be established. If, on adding  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ , is found present, heat must not be applied.

$\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$ , are liberated from their compounds.  $\text{SO}_2$  shows presence of sulphites or hyposulphites;  $\text{CO}$  of oxalates or cyanides.  $\text{HC}_2\text{H}_3\text{O}_2$ , set free and recognized by odor.  $\text{Br}_2$  and  $\text{I}_2$  liberated from bromides and iodides,  $\text{Cl}_2\text{O}_2$  from chlorates. Tartrates blacken.

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## SOLUTION.

### Treatment with Water

The substance in fine powder must be treated with water, first cold then hot. Most salts are more readily soluble in hot water than in cold; in a few cases the reverse is true, and some salts, though soluble in cold water, are decomposed by boiling water into insoluble basic salts. Salts of  $\text{Bi}$ , and some salts of  $\text{Sb}$ ,  $\text{Hg}$  and  $\text{Hg}_2$ , are thus decomposed even by cold water.

After boiling for some time, if a portion remains undissolved, it must be collected upon a filter, washed and treated with acids. If there be any doubt whether even a part of the substance is soluble, a few drops of the filtrate must be evaporated on platinum foil.

The reaction of the aqueous solution should be tested, or, if the substance under examination is liquid, the reaction of the original solution.

An alkaline reaction shows the presence of Gr. I. or II. An acid reaction may be due to the presence of a free acid or acid salt, or due to the presence of a neutral

salt with acid reaction. In the first case a drop of  $\text{Na}_2\text{CO}_3 + \text{Aq}$  gives no precipitate, or the precipitate which is formed redissolves; in the second the turbidity is usually permanent.

### Treatment with Acids.

For the solution of a substance insoluble in water  $\text{HCl} + \text{Aq}$ ,  $\text{HNO}_3$ , or a mixture of the two (aqua regia) is used. A solution in  $\text{HCl} + \text{Aq}$  is much the best for subsequent work.

Many substances are soluble in dilute acids, though insoluble in strong, many soluble only in strong, and again many, that are not attacked by dilute acids, are decomposed, though not dissolved, by stronger acids, so that solution can only be effected by treatment with strong acids and subsequent dilution. The substance should therefore be boiled successively with  $\text{HCl} + \text{Aq}$ ,  $\text{HNO}_3$ , and  $\text{HCl} + \text{Aq}$  with  $\text{HNO}_3$ , using first dilute, then strong, and finally adding water to that which has been boiled with strong acid.

Effervescence may show  $\text{CO}_2$  present, or if  $\text{HCl} + \text{Aq}$  is used  $\text{H}_2\text{S}$  or  $\text{SO}_2$ . With  $\text{HCl} + \text{Aq}$   $\text{HCN}$  is often set free from insoluble cyanides, or  $\text{Cl}_2$  is evolved if dioxides or chromates are present.  $\text{S}$  or gelatinous  $\text{H}_2\text{SiO}_4$  are also often separated. Unless  $\text{As}$  or  $\text{Sb}$  may be present, the solution should be freed from any great excess of acid by evaporation. It is much better, in any case, to avoid an excess from the first, taking care also that the solution be properly diluted before beginning the analysis.  $\text{HCl} + \text{Aq}$  and  $\text{HNO}_3$  together dissolve by converting into chlorides.

If the substance is a metal or alloy, as will appear in the preliminary examination, it should be treated at once with hot  $\text{HNO}_3$ —, 1 part strong acid to 3 of water. Sb and Sn are oxidized to  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_3$  ( $\text{Sb}_2\text{O}_3$ ) insoluble in water, or dilute  $\text{HNO}_3$ , the other metals are found in solution. As many nitrates are insoluble in strong  $\text{HNO}_3$ , though readily soluble in water, care must be taken not to mistake the crystalline nitrates for oxides of Sn or Sb. The insoluble residue may contain a part of any As present.

#### **Treatment of Substances Insoluble in Water or Acids.**

The most common substances insoluble in water or acids are :  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $(\text{CaSO}_4)$ ,  $\text{PbSO}_4$ ; the Ag salts of acids of Gr. II., except  $\text{Ag}_2\text{S}$ ; ignited  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  or  $\text{SnO}_2$ ;  $\text{SiO}_2$  and many silicates;  $\text{CaF}_2$ , S and C.

S is recognized in the preliminary examination. C is present if the substance is black, and part of it burns before the blowpipe. If Pb and Ag have not been found in the preliminary examination, special tests must be made for their presence. Ag may be found, if present, by warming the substance with  $\text{KCN} + \text{Aq}$ , which dissolves all the Ag salts insoluble in acids, and testing the filtrate with  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ . To test for Pb, warm the substance with  $\text{H}_4\text{NC}_2\text{H}_3\text{O}_2 + \text{Aq}$ , which dissolves  $\text{PbSO}_4$ , and add to the filtered solution  $(\text{H}_2\text{N})_2\text{S} + \text{Aq}$ . If Ag or Pb are present they must be removed by successive treatment with  $\text{H}_4\text{NC}_2\text{H}_3\text{O}_2 + \text{Aq}$ , and  $\text{KCN} + \text{Aq}$ . If S is also present, it must be volatilized in a porcelain crucible after the removal of Pb and Ag. If

S is present, cold KCN + Aq must be used for the removal of Ag.

The substance free from Ag, Pb and S, may then be mixed with 2 parts  $\text{Na}_2\text{CO}_3$ , 2 parts  $\text{K}_2\text{CO}_3$ , and 1 part  $\text{KNO}_3$ , and heated to quiet fusion in a platinum crucible. From the cooled mass water then dissolves alkaline salts of the acids present, and the bases are left as carbonates, soluble in  $\text{HCl} + \text{Aq}$ , after thorough washing. Al, is found in solution, and Cr, as chromate. To find the acids of the insoluble Ag salts,  $\text{NaOH} + \text{Aq}$ , dilute, will decompose the ferro- and ferricyanide, sodic salts of those acids going into solution by boiling;  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$  and  $\text{AgCN}$  are reduced by Zn and dilute  $\text{H}_2\text{SO}_4$ ; in the solution  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  and  $\text{HCN}$  may be found. If the members of Gr. I. must be looked for in silicates, fuse with 4 parts of  $\text{BaO.H}_2$ .

Some substances insoluble, or slowly soluble, in acids, may be decomposed with advantage by  $\text{NaOH} + \text{Aq}$ . The insoluble ferrocyanides and ferricyanides are decomposed by hot  $\text{NaOH} + \text{Aq}$ , into sodic salts of the acids and insoluble or soluble hydrates. The solution may therefore be examined for Pb, Zn and Al, and, after their removal, for the acids, although it must be remembered that  $\text{H}_4\text{Fe}_2(\text{CN})_{12}$  in the alkaline solution is readily converted into  $\text{H}_4\text{Fe}(\text{CN})_6$  by  $\text{H}_2\text{S}$ . The portion insoluble in  $\text{NaOH} + \text{Aq}$  may be dissolved in acids and tested as usual.

The three portions of any substance, that soluble in water, that soluble only in acids, and that insoluble in water and acids, must be separately examined. The larger portion should first be analyzed, inasmuch as a

knowledge of its constitution may greatly facilitate the analysis of the smaller portions.

### DETECTION OF BASES.

The bases may be divided according to their behavior with reagents into six groups, and, for convenience in analysis, these groups are separated from each other by general reagents before proceeding to test for the individual members of each group.<sup>1</sup> In an acid solution  $H_2S$  precipitates only members of Grs. V. and VI. The precipitation is complete, unless the solution is very strongly acid, in which case more or less Pb and Cd remain in solution. The sulphides of the two groups are separated by an alkaline solution, the sulphides of Gr. V. being insoluble, those of Gr. VI. soluble, but precipitated by the addition of acid. As the  $HCl + Aq$ , best used to acidify the solution, precipitates  $AgCl$ ,  $Hg_2Cl_2$ , and  $PbCl_2$  (partially), it is more convenient to separate these by filtration, and test for them apart. The members of Grs. III. and IV. are not precipitated by  $H_2S$  in a solution acidified with  $HCl + Aq$ , but are precipitated by  $(H_4N)_2S + Aq$  in an alkaline solution—Gr. III. as hydrates, Gr. IV. as sulphides. Grs. V. and VI. are also precipitated by  $(H_4N)_2S + Aq$ , though the precipitate of Gr. VI. redissolves in an excess. Grs. V. and VI. must therefore be removed before precipitating Grs. III. and IV. It is more convenient not to separate Gr. III. as a whole from Gr. IV., but to test the general precipitate for members of both groups. The members of Gr. II. are not precipitated by  $H_2S$  or  $(H_4N)_2S + Aq$ , and are distinguished from Gr.

<sup>1</sup> Compare table of bases on page 1

I. by the insolubility of their carbonates.  $(H_4N)_2CO_3 + Aq$  precipitates Ba, Sr and Ca as carbonates, but as Mg is not precipitated as carbonate in presence of  $H_4N$  salts, it is more convenient to make a special test for its presence, and remove it after the  $H_4N$  salts have been expelled by ignition.  $(H_4N)_2CO_3 + Aq$  precipitates most of the members of Grs. VI.-III., and these groups must therefore be removed before the precipitation of Gr. II. Members of Gr. I. are precipitated by no general reagent, but are left in solution after the removal of the higher groups. Since  $H_4N$  salts are used as reagents, tests for  $H_4N$  must be made in the original solution. ●

**GROUPS V. and VI.** Ag, Hg<sub>2</sub>, Pb, Hg, Cu, Bi, Cu; As, Sb, Sn, Sn<sup>IV</sup>.

To the solution add HCl + Aq. If a white precipitate<sup>1</sup> falls, it may contain AgCl, Hg<sub>2</sub>Cl<sub>2</sub> and PbCl<sub>2</sub>. Filter, wash the precipitate with a little cold water, and set aside the filtrate. The precipitate must then be washed with hot water; AgCl and Hg<sub>2</sub>Cl<sub>2</sub> are insoluble, PbCl<sub>2</sub> is dissolved, ● present, and by adding dilute H<sub>2</sub>SO<sub>4</sub> to the solution PbSO<sub>4</sub> is precipitated. The residue, which may consist of AgCl and Hg<sub>2</sub>Cl<sub>2</sub>, is next treated on the filter with H<sub>4</sub>NOH + Aq. Hg<sub>2</sub>Cl<sub>2</sub>, if present, is converted into black insoluble  $[Hg_2]_2H_4N_2Cl_2$ , and AgCl is dissolved. To the

<sup>1</sup> If the solution is alkaline, on the addition of HCl + Aq As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub> or SnS<sub>2</sub> may be precipitated; cyanides dissolved in KCN + Aq may be thrown down; gelatinous H<sub>2</sub>SiO<sub>3</sub> separated, or S from alkaline sulphides. CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and HCN may be set free. AgCl is soluble in Hg(NO<sub>3</sub>)<sub>2</sub> + Aq, but is precipitated by the addition of H<sub>4</sub>NC, H<sub>2</sub>O, + Aq.



$H_4NOH^1 + Aq$  which has run through the filter is then added  $HNO_3$  in excess; if Ag is present,  $AgCl$  is precipitated, white and curdy, or, if in small quantity, opalescent.

To the filtrate from the precipitate caused by  $HCl + Aq$ , add  $H_2S + Aq$ , or better, pass into it  $H_2S$ ; warm for some time, adding  $H_2S + Aq$  until the solution smells strongly of it after shaking, and filter. The filtrate, which may contain Grs. I.-IV. is set aside; the precipitate may contain  $PbS$ ,  $HgS$ ,  $CuS$ ,  $Bi_2S_3$ ,  $CdS$ ,  $As_2S_3$ ,  $Sb_2S_3$ ,  $SnS$  and  $SnS_2$ . It must be washed with hot water until  $AgNO_3$  gives no precipitate of  $AgCl$  in the wash water, and then gently warmed with very little yellow  $(H_4N)_2S + Aq$ . The sulphides of Gr. VI. are thus dissolved. Filter and set the filtrate aside to be examined for members of Group VI. The precipitate, which may contain  $PbS$ ,  $HgS$ ,  $CuS$ ,  $Bi_2S_3$ , and  $CdS$ , after being well washed, is boiled with dilute  $HNO_3$ .  $HgS$  alone is insoluble, although the S which separates is often colored with a little of one of the other sulphides, and a black residue must therefore be tested for Hg. The residue is filtered off, dissolved in  $HCl + Aq$  with the addition of a very little  $KClO_3$ , and bright bits of Cu wire put into the solution. Hg, if present, is deposited on the Cu, and when dried may be sublimed in a bulb tube. The  $HNO_3$  solution filtered from  $HgS$  or separated S may contain the nitrates of Pb, Cu, Bi and Cd. If Pb has already been found, it must be removed, and if not found, it may yet be present in quantity too small to be precipitated by  $HCl + Aq$ . The solution must be

<sup>1</sup> If  $PbCl_2$  is not completely washed out, the  $H_4NOH + Aq$  is often turbid from the presence of a basic Pb salt. This does not interfere with the detection of Ag, as it dissolves readily in  $HNO_3$ .

concentrated by evaporation until the greater part of the  $\text{HNO}_3$  has been driven off, dilute  $\text{H}_2\text{SO}_4$  added, the solution gently warmed and allowed to stand for some time.

A white precipitate is  $\text{PbSO}_4$  and shows Pb present. If Pb is present, the solution must be evaporated with dilute

?  $\text{H}_2\text{SO}_4$  until the  $\text{HNO}_3$  is all expelled, water slightly acid with  $\text{H}_2\text{SO}_4$  added, and the insoluble  $\text{PbSO}_4$  filtered off.

The solution now may contain Cu, Bi and Cd. Add  $\text{H}_2\text{NOH} + \text{Aq}$  in excess, which precipitates  $\text{BiO}_2\text{H}_3$ , white and flocculent, if Bi is present; if the solution is blue, Cu is present. Filter from the precipitated  $\text{BiO}_2\text{H}_3$ . If the

filtrate is not blue, a very small quantity of Cu may be detected by acidifying a portion with  $\text{HCl}$ ,  $\text{H}_2\text{O}$ , and adding  $\text{K}_2\text{Fe}(\text{CN})_6 + \text{Aq}$  which precipitates red brown  $\text{Cu}_2\text{Fe}(\text{CN})_6$ .

If Cu is absent,  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  added will precipitate yellow  $\text{CdS}$ . If Cu is present, precipitate CuS and CdS with  $\text{H}_2\text{S} + \text{Aq}$ , and boil the mixed sulphides with

dilute  $\text{H}_2\text{O}$ , avoiding exposure to the air. CdS, if present, is alone dissolved, and, after filtering off the undissolved CuS, may be precipitated by  $\text{H}_2\text{S}$ , or  $\text{H}_2\text{NOH} + \text{Aq}$  and  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ , as yellow CdS.

The  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  solution which may contain Gr. VI. is acidified with dilute  $\text{HCl} + \text{Aq}$ . The sulphides are thus precipitated mixed with S. If too much  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  was not used for solution, the presence of the sulphides is readily recognized. The precipitate, which may contain  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{SnS}_2$ , is collected on a filter and washed, then treated in the cold with  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$ .  $\text{As}_2\text{S}_3$  dissolves and may be precipi-

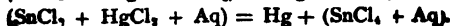
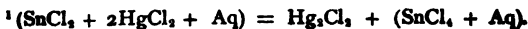
<sup>1</sup> Brown SnS dissolved in yellow  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  is precipitated by  $\text{HCl} + \text{Aq}$  as yellow  $\text{SnS}_2$ .

tated from the filtered solution by acidifying with HCl + Aq as yellow  $\text{As}_2\text{S}_3$ , if As is present. In order to confirm the presence of As, the precipitate must be thoroughly dried, mixed with dry KCN and  $\text{Na}_2\text{CO}_3$ , and the mixture heated in a bulb tube; As, if present, is sublimed as a metallic mirror.

The residue insoluble in  $(\text{H}_4\text{N})_2\text{CO}_3$  + Aq may contain  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$ . It is dissolved in strong HCl + Aq, with the addition of a little  $\text{KClO}_3$ , if necessary; any large excess of HCl + Aq must be avoided. The solution is diluted and into it are put bits of platinum foil and Zn in contact. When the evolution of  $\text{H}_2$  has ceased, Sb and Sn, if present, are found deposited upon the foil, Sb black, and Sn silver white. The foil must be carefully washed and warmed with HCl + Aq. Sn, if present, is dissolved as  $\text{SnCl}_2$ , which may be recognized in solution by adding  $\text{HgCl}_2$  + Aq;  $\text{Hg}_2\text{Cl}_2$  being precipitated, often gray from Hg.<sup>1</sup> Sb may be recognized by the black color of the foil. If confirmation is needed, it may be dissolved in  $\text{H}_2\text{C}_2\text{H}_3\text{O}_4$  + Aq with the addition of a few drops of  $\text{HNO}_3$ ; from this solution  $\text{H}_2\text{S}$  precipitates, after addition of HCl + Aq, orange,  $\text{Sb}_2\text{S}_3$ , if Sb is present.

**Groups III. and IV.—Al., Cr., Fe., Fe., Ni, Co, Mn, Zn,**  
and phosphates and oxalates soluble in acids only.

To the filtrate from the general precipitate of Grs. V. and VI., or to the solution found not to contain Grs. V. and VI., add  $\text{H}_4\text{NCl}$  + Aq and  $\text{H}_4\text{NOH}$  + Aq in slight excess; heat almost to boiling, add  $(\text{H}_4\text{N})_2\text{S}$  and keep



warm for some time. The precipitate is more granular if the solution is shaken well in a corked flask. Filter as rapidly as possible and wash with hot water, best with addition of a little  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ . The filtrate, which may contain Grs. I. and II.,<sup>1</sup> must be concentrated by evaporation, filtered if necessary, and set aside. The color of the precipitate gives some indication of what is present. It may contain  $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}$ ,  $\text{FeS}$ ,  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{NiS}$ , or  $\text{CoS}$ , together with phosphates or oxalates of  $\text{Al}$ ,  $\text{Cr}$ , and  $\text{Gr. II.}$ , and must be tested for all, if it is black. First treat with cold dilute  $\text{HCl} + \text{Aq}$ ;  $\text{NiS}$  and  $\text{CoS}$  alone are insoluble, the rest go into solution. If a black residue remains  $\text{Ni}$  or  $\text{Co}$ , or both, are present. The residue must be collected on a filter and tested for  $\text{Co}$  with borax. A blue bead in the inner and outer flames shows  $\text{Co}$  is present, and  $\text{Ni}$  may be. If  $\text{Co}$  is absent and the bead gives the  $\text{Ni}$  reactions, the black residue was  $\text{NiS}$ . If  $\text{Co}$  is present, dissolve in  $\text{HCl} + \text{Aq}$  and  $\text{HNO}_3$ , add  $\text{NaOH} + \text{Aq}$  in excess and filter. Dissolve the hydrates thus obtained in as little as possible concentrated  $\text{KCN} + \text{Aq}$ , add  $\text{NaOH} + \text{Aq}$  and  $\text{Br}_2 + \text{Aq}$ . On boiling  $\text{Ni}$ , if present, is precipitated as  $\text{Ni}_2\text{O}_3\cdot\text{H}_2\text{O}$ ,  $\text{Co}$  remains in solution as  $\text{Na}_2\text{Co}_2(\text{CN})_{12}$ . Co.

The solution in  $\text{HCl} + \text{Aq}$ , filtered from  $\text{NiS}$  or  $\text{CoS}$ , if a residue was left, is boiled until  $\text{H}_2\text{S}$  is all expelled, a little  $\text{HNO}_3$  is added, the solution again boiled till the greater part of the acid is driven off and then diluted with

<sup>1</sup> If  $\text{Ni}$  is present more or less  $\text{NiS}$  is dissolved in the excess of  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ , especially if much  $\text{H}_2\text{NOH} + \text{Aq}$  is added; the filtrate is then brown or black. By evaporating and acidifying with  $\text{HCl}$ ,  $\text{H}_2\text{O}$ , or  $\text{HCl} + \text{Aq}$ ,  $\text{NiS}$  is precipitated. // // //

water. If it is not already known whether  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  are present or not, this must now be determined.

If  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  are absent, neutralize the little free acid in the solution with  $\text{Na}_2\text{CO}_3$ , care being taken that no permanent precipitate is formed, then add  $\text{BaCO}_3$  in the cold and allow the whole to stand for some time, stirring occasionally. The precipitate may contain  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , or  $\text{Fe}_2\text{O}_3$ , together with the excess of  $\text{BaCO}_3$ , the filtrate may contain Mn or Zn with  $\text{BaCl}_2$ . Dissolve the precipitate collected on a filter in dilute  $\text{HCl} + \text{Aq}$ , ~~heat gently~~ and add  $\text{H}_2\text{NOH} + \text{Aq}$  which will precipitate as hydrates  $\text{Fe}$ ,  $\text{Al}$ , and  $\text{Cr}$ , if present. This precipitate must be collected on a filter, washed, dried and dissolved in a little strong  $\text{HNO}_3$ . The solution is then boiled with a few crystals of  $\text{KClO}_4$  for several minutes, and  $\text{NaOH} + \text{Aq}$  added in excess.  $\text{Fe}_2\text{O}_3$  is precipitated, if Fe is present, and the solution may contain  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{CrO}_4$ . In a part of the solution  $\text{Al}$  may be precipitated by adding  $\text{H}_2\text{NCl} + \text{Aq}$  as  $\text{Al}_2\text{O}_3$ ,<sup>1</sup> or, after acidifying with  $\text{HNO}_3$ ,  $\text{H}_2\text{NOH} + \text{Aq}$  causes the same precipitate; another portion of the solution is acidified with  $\text{HCl}$ ,  $\text{H}_2\text{O}$ , and  $\text{BaCl}_2 + \text{Aq}$  added, which precipitates  $\text{BaCrO}_4$ , if Cr, is present. If  $\text{NaOH} + \text{Aq}$  precipitates  $\text{Fe}_2\text{O}_3$ , the original solution must be tested by adding to a small portion  $\text{K}_2\text{Fe}(\text{CN})_6 + \text{Aq}$ , which gives blue  $\text{Fe}_3\text{Fe}(\text{CN})_{12}$  if Fe is present;

<sup>1</sup>  $\text{NaOH}$  often contains silicate, and gelatinous  $\text{H}_2\text{SiO}_3$  is then precipitated here. It may be distinguished from  $\text{Al}_2\text{O}_3$ , by its insolubility in  $\text{H}_2\text{NNaHPO}_4$ , bead, and readily separated from it by fusion with  $\text{KHSO}_4$ , treatment with  $\text{HCl} + \text{Aq}$  and precipitation of  $\text{Al}_2\text{O}_3$ , from the solution, if present, by  $\text{H}_2\text{NOH} + \text{Aq}$ .

to another portion add  $K_4Fe(CN)_6$  + Aq, which gives blue  $[Fe_3][Fe(CN)_6]_4$ , or KCNS giving blood red solution of  $Fe_3(CNS)_6$ , if Fe, is present.

Small quantities of Cr, may also be detected by fusing the dried precipitate with a mixture of equal parts of  $Na_2CO_3$  and  $KNO_3$ . If the cooled mass is boiled with water, the solution filtered and acidified with  $H_2C_2O_4$ , on the addition of  $Pb(C_2H_3O_2)_2$  + Aq,  $PbCrO_4$  is precipitated.

The filtrate from the  $BaCO_3$  precipitate, which may contain Zn and Mn, is heated to boiling and the Ba it contains completely precipitated with dilute  $H_2SO_4$ ; filter from the  $BaSO_4$ , to the filtrate add NaOH + Aq in excess ~~and boil~~.  $MnO_2 \cdot H_2O$  is precipitated, if present, and the solution may contain Zn. The precipitate is collected on a filter, and a portion of it fused on platinum ~~wire~~ with  $Na_2CO_3$  and  $KNO_3$ . Blue green  $K_2MnO_4$  is formed, if the precipitate was  $MnO_2 \cdot H_2O$ . The NaOH + Aq solution, which may contain Zn, is acidified with  $H_2C_2O_4$  and ZnS, white, precipitated by  $H_2S$ , if Zn is present.

If  $H_3PO_4$  and  $H_2C_2O_4$  are present, the HCl + Aq solution boiled with  $HNO_3$ , and treated as before must first be tested for Ba, Sr and Ca. To a small portion add dilute  $H_2SO_4$ . If a precipitate is formed filter, and examine in the spectroscope. To the filtrate add 3 times its volume of alcohol;  $CaSO_4$  is precipitated, if Ca is present, and its presence may be confirmed by dissolving the precipitate in water and throwing down  $CaC_2O_4$  with  $(H_4N)_2C_2O_4$  + Aq. To the rest of the solution add  $FeCl_3$  + Aq cautiously till a drop of the solution gives with  $H_4NOH$  + Aq a yellowish precipitate. The solution must

then be neutralized with  $\text{Na}_2\text{CO}_3 + \text{Aq}$ , as before, and  $\text{BaCO}_3$  added. The precipitate with  $\text{BaCO}_3$  is examined as above, except, of course, that Fe and  $\text{Fe}_2$  must be proved present or absent by  $\text{H}_4\text{Fe}(\text{CN})_6 + \text{Aq}$  and  $\text{K}_3\text{Fe}_2(\text{CN})_6 + \text{Aq}$  in the original solution. The filtrate from the  $\text{BaCO}_3$  precipitate may contain Ca and Mg as well as Mn and Zn. After removing Ba with dilute  $\text{H}_2\text{SO}_4$ ,  $\text{H}_4\text{NOH} + \text{Aq}$  must be added, ZnS and MnS precipitated, if present, by  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ , collected on a filter, and dissolved in  $\text{HCl} + \text{Aq}$ . They may then be separated and detected as before. The filtrate from the precipitate of ZnS and MnS may contain Ca and Mg. The Ca is precipitated as  $\text{CaC}_2\text{O}_4$  filtered off, and the filtrate tested for Mg by adding  $\text{Na}_2\text{HPO}_4 + \text{Aq}$ .

#### GROUP II. Ba, Sr, Ca, Mg.

To the filtrate from the general precipitate of Grs. III. and IV., or to the solution found not to contain Grs. III.-VI., add  $\text{H}_4\text{NCl} + \text{Aq}$ ,<sup>1</sup> if it be not already in solution, then  $\text{H}_4\text{NOH} + \text{Aq}$  in slight excess, unless the solution is already alkaline; heat almost to boiling, add  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$  to complete precipitation, and filter after allowing it to stand for a few minutes.

The filtrate may contain Mg or members of Gr. I. To a small part of it add  $\text{Na}_2\text{HPO}_4 + \text{Aq}$ . A white crystalline precipitate, forming only after the lapse of some time, if the solution be dilute, is  $\text{Mg}_3(\text{H}_4\text{N})_6(\text{PO}_4)_2$ .<sup>2</sup> The rest of the filtrate is then evaporated for Gr. I.

<sup>1</sup>  $\text{H}_4\text{NCl} + \text{Aq}$  prevents possible precipitation of Mg.

<sup>2</sup> The filtrate may contain small quantities of Ba, Sr or Ca. A slight precipitate with  $\text{Na}_2\text{HPO}_4$  may therefore not be due to presence of Mg. In a fresh portion Ba should be tested for and removed

The precipitate thrown down by  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$  may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , or  $\text{CaCO}_3$ , and must be tested for all three. The carbonates are dissolved in  $\text{HC}_2\text{H}_3\text{O}_2$ , and to a small part of the solution  $\text{CaSO}_4 + \text{Aq}$  is added. An immediate white precipitate is  $\text{BaSO}_4$ , and shows that Ba is present,—Ca and Sr may be; a tardy precipitate is  $\text{SrSO}_4$ , and shows that Ba is absent and Sr present,—Ca may be; no precipitate even on long standing shows that Ba and Sr are absent, and the original precipitate was  $\text{CaCO}_3$  alone.

If Ba is present, it must be removed before testing for Sr or Ca. To the rest of the  $\text{HC}_2\text{H}_3\text{O}_2$  solution is then added  $\text{K}_2\text{CrO}_4 + \text{Aq}$  in slight excess, and the precipitated  $\text{BaCrO}_4$  filtered off. To the filtrate add  $\text{H}_4\text{NOH} + \text{Aq}$  in excess, warm and add  $(\text{H}_4\text{N})_2\text{CO}_3 + \text{Aq}$ . The precipitate may contain  $\text{SrCO}_3$ , or  $\text{CaCO}_3$ , or both. It must be washed till all  $\text{K}_2\text{CrO}_4$  is removed, and dissolved in  $\text{HC}_2\text{H}_3\text{O}_2$ . To a small portion of the solution add  $\text{CaSO}_4 + \text{Aq}$ . A white precipitate on standing is  $\text{SrSO}_4$  and shows Sr present,—Ca may be.

If Sr is present, to the rest of the  $\text{HC}_2\text{H}_3\text{O}_2$  solution, from which the Ba has been removed, or in which it was originally found absent, is added, dilute  $\text{H}_2\text{SO}_4$  in slight excess. After standing for some time  $\text{SrSO}_4$  separates, mixed with  $\text{CaSO}_4$ , if the solution is concentrated; on filtering  $\text{CaSO}_4$  will be found in solution, if present, by adding  $\text{H}_4\text{NOH} + \text{Aq}$  in excess and  $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4 + \text{Aq}$ ; Ca then falls as white  $\text{CaC}_2\text{O}_4$ .

If Sr is absent, whether Ba was originally absent or was with dilute  $\text{H}_2\text{SO}_4$ , Ca with  $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4 + \text{Aq}$  before accepting the precipitate with  $\text{Na}_2\text{HPO}_4 + \text{Aq}$  as a proof of the presence of Mg.



removed,  $\text{H}_4\text{NOH} + \text{Aq}$  and  $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$  added to the rest of the  $\text{HC}_2\text{H}_3\text{O}_2$  solution precipitates  $\text{CaC}_2\text{O}_4$  if Ca is present.

Ba, Sr and Ca may also be distinguished by the spectro-scope. Ba recognized by four green bands; Sr by one orange, two red, and one blue band; Ca best by a green and orange band.

### GROUP I. Na, K, Li, HN.

The filtrate from the general precipitate of Gr. II. or the solution in which Grs. II.-VI. have been found absent, must be evaporated to dryness and ignited until  $\text{H}_4\text{N}$  salts are expelled.

If Mg was found to be absent, the residue contains only Na, K or Li, and should be tested with the spectro-scope. K gives a band in the extreme red, Na a yellow band, and Li a red band between the two. The presence of Na in notable quantity is shown by the intensity and duration of the yellow flame.  $\text{NaHC}_2\text{H}_3\text{O}_2 + \text{Aq}$  may also be used in a cold concentrated aqueous solution of the residue as a test for K, precipitating  $\text{KHC}_2\text{H}_3\text{O}_2$ .  $\text{NaC}_2\text{O}_4 + \text{Aq}$  precipitates from concentrated solutions.  $\text{LiCO}_3$ , or  $\text{Na}_2\text{HPO}_4 + \text{Aq}$ , with the addition of a little  $\text{NaOH} + \text{Aq}$ , precipitates  $\text{Li}_2\text{PO}_4$  in a solution not too dilute.

If Mg was found present, the residue from ignition<sup>1</sup> must be dissolved in a little water, and  $\text{BaO}_2\text{H}_2 + \text{Aq}$  added in slight excess. The  $\text{MgO}_2\text{H}_2$  thus precipitated is filtered out, the Ba completely precipitated from the boiling hot filtrate by dilute  $\text{H}_2\text{SO}_4$ , and the liquid freed

<sup>1</sup>  $\text{MgO}_2\text{H}_2$  not precipitated from solutions containing  $\text{H}_4\text{N}$  salts.

from  $\text{BaSO}_4$  by filtration evaporated to dryness. The residue, after the excess of  $\text{H}_2\text{SO}_4$  has been driven off, is tested as before in the spectroscopic.

To test for  $\text{H}_4\text{N}$  some of the original solution or substance must be mixed with  $\text{CaO}, \text{H}_2\text{O}$ , to a stiff paste, and gently warmed.  $\text{H}_4\text{N}^1$  is then set free, which may be recognized by its action on moist test-paper, or by its forming white fumes of  $\text{H}_4\text{NCl}$  with  $\text{HCl}^2$ .

### DETECTION OF ACIDS.

The acids are divided into three groups, according to the solubility of the Ba and Ag salts.<sup>3</sup>  $\text{BaCl}_2 + \text{Aq}$  precipitates all the members of Gr. I. in neutral or alkaline solutions, but does not precipitate Grs. II. and III.  $\text{AgNO}_3 + \text{Aq}$  precipitates in  $\text{HNO}_3$  solution only members of Gr. II., but in neutral solution almost all of Gr. I. Members of Gr. III. are precipitated by neither reagent. The acids are not separated after precipitation by the general reagents, as was the case with bases, the presence or absence of members of the groups alone being shown.

In beginning the analysis for acids, those acids, which from the nature of the bases present and the solvent used are necessarily absent, must first be considered. In a substance soluble in water no acids can be present which form insoluble salts with any of the bases found in the solution. In a substance insoluble in water and

<sup>1</sup>  $2\text{H}_4\text{NCl} + \text{CaO}, \text{H}_2\text{O} = \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{H}_4\text{N}.$

<sup>2</sup> The  $\text{HCl} + \text{Aq}$  used must not fume in the air.

See table of acids on page 19.

soluble in acids, the number of acids which may thus be safely excluded, as forming soluble salts with the bases is small, and it is better to look for all. In substances insoluble in water or acids, a knowledge of the bases will usually render the number of acids that must be tested for very small.

If the substance is soluble in water, the bases will generally not interfere with the detection of those acids which can be present, although in testing for  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  the solution cannot contain bases of Grs. III.-VI. If the substance is soluble in acids alone, the removal of the bases of Grs. III.-VI. always facilitates the detection of the acids, and is often essential. They should be removed with  $\text{H}_2\text{S}$ ,  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$ ,  $\text{Na}_2\text{CO}_3 + \text{Aq}$ ,  $\text{NaOH} + \text{Aq}$ , as the case may be, any excess of  $\text{H}_2\text{S}$  removed, and the solution made neutral, carefully boiling out  $\text{CO}_2$ , if  $\text{Na}_2\text{CO}_3$  was used.

#### GROUP I. 1. $\text{M.CrO}_3$ , $\text{M.AsO}_3$ , $\text{H.AsO}_3$ , $\text{M.SO}_3$ , $\text{M.S.O}_3$ .

These acids will have been discovered, if present, by the preliminary examination, or in the course of the analysis for bases; their presence must be confirmed by special tests. They are all decomposed by  $\text{H}_2\text{S}$  in acid solution.

**Chromates.**— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Aq}$  gives yellow  $\text{PbCrO}_4$ , insoluble in  $\text{HC}_2\text{H}_3\text{O}_2$ .  $\text{AgNO}_3 + \text{Aq}$  in neutral solution precipitates brick red  $\text{AgCrO}_4$ .

**Arsenites.**— $\text{H}_2\text{S}$  precipitates  $\text{As}_2\text{S}_3$  yellow immediately from acid solutions;  $\text{AgNO}_3 + \text{Aq}$  gives in neutral solutions pale yellow  $\text{Ag}_3\text{AsO}_3$ . Further recognized in presence of  $\text{H}_2\text{AsO}_4$  by adding a few drops of  $\text{CuSO}_4$ .

+ Aq, then NaOH + Aq in excess ; on boiling  $\text{Cu}_2\text{O}, \text{H}_2$  precipitated, orange yellow.

**Arsenates.**— $\text{H}_2\text{S}$  precipitates  $\text{As}_2\text{S}_3$  very slowly from acid solutions ;  $\text{AgNO}_3$  + Aq gives in neutral solutions red brown precipitate of  $\text{Ag}_3\text{AsO}_4$ . Further distinguished from arsenites by  $\text{H}_2\text{NOH}$  + Aq,  $\text{H}_2\text{NCl}$  + Aq and  $\text{MgSO}_4$  + Aq ;  $\text{Mg}_3(\text{H}_2\text{N})_2(\text{AsO}_4)_2$  precipitated, easily mistaken for phosphate.

**Sulphites.**—Salts give off  $\text{SO}_2$  when treated with  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  + Aq.  $\text{SO}_2$  recognized by smell and blackening of paper moistened with  $\text{Hg}_2(\text{NO}_3)_2$  + Aq by separation of Hg. Zn and  $\text{HCl}$  + Aq liberate from solutions of sulphides  $\text{H}_2$  mixed with  $\text{H}_2\text{S}$ . If sulphides also present, must they be removed by  $\text{ZnSO}_4$  + Aq and the filtrate tested.

**Hyposulphites.**—From solutions  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  + Aq evolve  $\text{SO}_2$  with separation of S. The reaction is delayed by dilution.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  + Aq or  $\text{AgNO}_3$  + Aq give white precipitates which blacken on boiling.<sup>1</sup> Sulphides, if present, must first be removed with  $\text{ZnSO}_4$  + Aq.

**GROUP I.** 2. (a)  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{HC}_2\text{O}_4$ ,  $\text{HF}$ ,  $\text{M}_2\text{CO}_3$ ,  $\text{H}_2\text{SiO}_3$ ,  $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ ; (b)  $\text{H}_2\text{SO}_4$ .

By the preliminary examination  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ , and  $\text{H}_2\text{SiO}_3$  will have been found, if present.  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{SiO}_3$  must be removed by  $\text{HCl}$  + Ag or  $\text{HNO}_3$  and evaporation, if present ; their presence is confirmed by special tests.

To a solution free from acids of Gr. I. 1,  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{SiO}_3$ , add  $\text{H}_2\text{NOH}$  + Aq to neutral or slightly alkaline reaction, then  $\text{BaCl}_2$  + Aq. The precipitate may contain



the Ba salts of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HF}$ ,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ , and  $\text{H}_2\text{SO}_4$ . Add dilute <sup>1</sup>  $\text{HCl} + \text{Aq}$  in excess;  $\text{BaSO}_4$  is insoluble, the other Ba salts dissolve. If  $\text{H}_4\text{NOH} + \text{Aq}$  is added in excess to the filtered solution,  $\text{Ba}_3(\text{PO}_4)_2$  and  $\text{BaC}_2\text{O}_4$  are precipitated, if present; the other Ba salts, more or less soluble in  $\text{H}_4\text{NCl} + \text{Aq}$ , will probably not be precipitated, if present. If therefore  $\text{H}_4\text{NOH} + \text{Aq}$  causes a precipitate in the  $\text{HCl} + \text{Aq}$  solution, special tests must be made for all the acids, except  $\text{H}_2\text{SO}_4$ , whose presence or absence is already established; if  $\text{H}_4\text{NOH}$  gives no precipitate,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  are absent, and for the rest special tests must be applied.

It is often advisable to add  $\text{CaCl}_2 + \text{Aq}$  to a fresh portion of the solution made slightly alkaline with  $\text{H}_4\text{NOH} + \text{Aq}$ . The Ca salts of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HF}$  and  $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$  are thus precipitated;  $\text{CaSO}_4$  is not thrown down, if the solution is moderately dilute. Of these Ca salts  $\text{CaC}_2\text{O}_4$  and  $\text{CaF}_2$  alone are insoluble in  $\text{HC}_2\text{H}_3\text{O}_2$ ; if the precipitate is soluble in  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{HF}$  are absent, if insoluble all may be present.

**Phosphates.**—In aqueous solutions  $\text{H}_4\text{NOH} + \text{Aq}$ ,  $\text{H}_4\text{NCl} + \text{Aq}$  and  $\text{MgSO}_4 + \text{Aq}$  precipitate crystalline  $\text{Mg}_3(\text{H}_4\text{N})_2(\text{PO}_4)_2$ , which appears only after some time, if the solution is dilute. To detect  $\text{H}_3\text{PO}_4$  in salts soluble in acids alone, add a little of a  $\text{HNO}_3$  solution of the salt to  $(\text{H}_4\text{N})_2\text{MO}_4$  dissolved in  $\text{HNO}_3$ ; a yellow precipitate is formed at once, or on gently warming (not above  $40^\circ$ ), if the solution is very dilute.  $\text{H}_3\text{AsO}_4$  gives a similar precipitate on boiling.

<sup>1</sup>  $\text{BaCl}_2$  is insoluble in strong  $\text{HCl} + \text{Aq}$ .

**Borates.**—Into a solution acid with  $\text{HCl} + \text{Aq}$  is dipped a strip of turmeric paper. The paper when dried at  $100^\circ$  is red, the red tint changing to greenish black on moistening with  $\text{Na}_2\text{CO}_3 + \text{Aq}$ .

**Oxalates.**—Distinguished from phosphates by the insolubility of  $\text{CaC}_2\text{O}_4$  in  $\text{HC}_2\text{H}_3\text{O}_2$ , and by giving no precipitate with  $\text{MgSO}_4 + \text{Aq}$  in presence of  $\text{H}_4\text{NCl} + \text{Aq}$ . The salts heated with strong  $\text{H}_2\text{SO}_4$  evolve  $\text{CO}$  and  $\text{CO}_2$ . The  $\text{CO}$  may be kindled, if in sufficient quantity; dilute  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  set free  $\text{CO}_2$ . The insoluble oxalates of Gr. II. give, when boiled with a concentrated solution of  $\text{Na}_2\text{CO}_3$ , an insoluble carbonate and  $\text{Na}_2\text{C}_2\text{O}_4$  in solution.

**Fluorides.**—The salt mixed with just enough strong  $\text{H}_2\text{SO}_4$  to form a thick paste is warmed in a platinum crucible covered with a piece of glass.  $\text{HF}$  is set free and the glass is etched. The etching is best seen, if the glass is covered with wax, and a few scratches made through it. If  $\text{Si}$  is present,  $\text{SiF}_4$  is evolved. Compounds of  $\text{F}$ , upon which  $\text{H}_2\text{SO}_4$  has no action, must be fused with a mixed  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ,  $\text{CaF}_2$  precipitated, and tested as before.

**Tartrates.**—The presence of tartrates is first recognized in the preliminary examination by charring with odor of burnt sugar.  $\text{CaC}_4\text{H}_4\text{O}_6$  is distinguished by its dissolving in cold  $\text{NaOH} + \text{Aq}$ ; when the solution is boiled the salt is thrown down as a gelatinous precipitate, which redissolves as the solution cools. In a solution acid with  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{KC}_2\text{H}_3\text{O}_2$  precipitates  $\text{KHC}_4\text{H}_4\text{O}_6$ .

**Carbonates.**—Salts decomposed by acids with effervescence, the escaping  $\text{CO}_2$  precipitates  $\text{CaCO}_3$  from

$\text{CaO}_2\text{H}_2 + \text{Aq. HCl} + \text{Aq}$  is poured upon the carbonate in a test tube, the gas allowed to collect and carefully decanted into another tube half full of  $\text{Ca}_2\text{O}_2\text{H}_2 + \text{Aq}$ . An excess of  $\text{CO}_2$  dissolves  $\text{CaCO}_3$  forming soluble  $\text{CaH}_2(\text{CO}_3)_2$ .

**Silicates.**—Generally recognized by the separation of gelatinous  $\text{H}_4\text{SiO}_4$  on adding  $\text{HCl} + \text{Aq}$ . A solution of a silicate acidified with  $\text{HCl} + \text{Aq}$  and evaporated to dryness leaves all its Si as a hard gritty powder insoluble in water or  $\text{HCl} + \text{Aq}$ . The powder is also insoluble in a bead of  $\text{NaH}_2\text{NHPO}_4$ ;  $\text{Al}_2\text{O}_3$  dissolves readily.

**Sulphates.**—Sufficiently characterized by  $\text{BaSO}_4$ ; insoluble in dilute  $\text{HCl} + \text{Aq}$ . Ignited on charcoal with  $\text{Na}_2\text{CO}_3$  in the inner blowpipe flame,  $\text{Na}_2\text{S}$  is formed, which, when moistened with water, stains Ag black.

**GROUP II.  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_4\text{Fe}(\text{CN})_6$ ,  $\text{H}_4\text{Fe}(\text{CN})_6$ .**

The presence of  $\text{H}_2\text{S}$  will have been already established, and probably that of  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  and  $\text{HCN}$ .  $\text{H}_2\text{S}$ , if present, must be expelled. As the Ag salts of all the acids of Gr. II except  $\text{AgF}$  are insoluble in water and soluble in  $\text{HNO}_3$ , acidify the solution with  $\text{HNO}_3$  and add  $\text{AgNO}_3 + \text{Aq}$ . The precipitate may contain Ag salts of all the members of the group. They are soluble in  $\text{H}_2\text{NOH} + \text{Aq}$ , except  $\text{AgI}$  and  $\text{Ag}_4\text{Fe}(\text{CN})_6$ . Further than this special tests must be made.

**Chlorides.**—On heating with  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ,  $\text{Cl}_2$  evolved, recognized by color, odor and bleaching power.  $\text{HCl}$  in the presence of  $\text{HBr}$  and  $\text{HI}$  may be recognized by adding to the hot solution  $\text{AgNO}_3 + \text{Aq}$  in quantity

insufficient to cause complete precipitation. If the filtered solution no longer contains HI or HBr, and  $\text{AgNO}_3 + \text{Aq}$  causes a further precipitate, HCl is present, since AgCl is last thrown down.

**Bromides.**—On heating with  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ,  $\text{Br}_2$  is evolved. To a solution of a bromide in a test tube add a little  $\text{CS}_2$  or chloroform, then  $\text{Cl}_2 + \text{Aq}$  drop by drop, shaking the tube; the liberated  $\text{Br}_2$  dissolves in the  $\text{CS}_2$ , coloring it red. If HI is also present the  $\text{CS}_2$  is violet. Add then  $\text{Cl}_2 + \text{Aq}$ , cautiously shaking the tube, and the violet  $\text{I}_2$  color will gradually disappear, and leave the  $\text{CS}_2$  colored red by  $\text{Br}_2$ —more  $\text{Cl}_2 + \text{Aq}$  will bleach the  $\text{Br}_2$  color also.

**Iodides.**—To a neutral or slightly acid solution of an iodide add a little thin boiled starch paste, and then  $\text{Cl}_2 + \text{Aq}$  cautiously. A blue compound of I with starch is formed. The color fades with heat or with an excess of  $\text{Cl}_2 + \text{Aq}$ . Instead of  $\text{Cl}_2 + \text{Aq}$ ,  $\text{KNO}_3 + \text{Aq}$ , in a solution acid with  $\text{H}_2\text{SO}_4$ , may be used to advantage, as an excess does little harm.

**Cyanides.**—Free HCN liberated from cyanides may be recognized by its odor (vapors poisonous). If a few drops of yellow  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  be exposed to the vapors of HCN or added to a liquid containing HCN,  $\text{H}_4\text{NCNS}$  is formed. The  $(\text{H}_4\text{N})_2\text{S} + \text{Aq}$  or the solution is evaporated until the excess of  $(\text{H}_4\text{N})_2\text{S}$  is driven off (not heated above  $100^\circ$ ), dilute  $\text{HCl} + \text{Aq}$  added and blood red  $\text{Fe}_3(\text{CNS})_4$  formed in solution by adding  $\text{Fe}_2\text{Cl}_6 + \text{Aq}$ . To a solution of HCN, or a cyanide, add successively  $\text{Fe}_2\text{SO}_4 + \text{Aq}$ ,  $\text{Fe}_2\text{Cl}_6 + \text{Aq}$ ,  $\text{NaOH} + \text{Aq}$  and  $\text{HCl} + \text{Aq}$  in excess: there is formed blue insoluble  $[\text{Fe}_2]_3[\text{Fe}(\text{CN})_6]_3$ .



**Sulphides.**— $H_2S$  is liberated by  $HCl + Aq$  from those sulphides which are decomposed by it. Paper moistened with  $Pb(C_2H_3O_2)_2 + Aq$ , best slightly alkaline, is blackened by exposure to  $H_2S$ ,  $PbS$  formed. From those sulphides not attacked by  $HCl + Aq$ ,  $HNO_3$  or  $HCl + Aq$  and  $HNO_3$  separate  $S$ , which is yellow and often spongy, and burns to  $SO_2$ . More or less  $H_2SO_4$  also formed.

**Ferrocyanides.**—Soluble salts recognized by giving on addition of  $Fe_2Cl_6 + Aq$ , blue  $[Fe_2]_3[Fe(CN)_6]_3$ . Insoluble salts boiled with  $NaOH + Aq$  and the acidified solution tested with  $Fe_2Cl_6 + Aq$ .

**Ferricyanides.**—Soluble salts, recognized by adding  $FeSO_4 + Aq$ —best made from dilute  $H_2SO_4$  and  $Fe$  to insure absence of  $Fe_2$  salt. Blue  $Fe_3Fe_2(CN)_{11}$  formed. Insoluble salts treated like the insoluble ferrocyanides, and the solution tested with  $FeSO_4 + Aq$ .

### GROUP III. $HNO_3$ , $HClO_3$ , $HCl.H.O.$ .

The acids will have been recognized in the preliminary examination; to confirm their presence special tests must be made.

**Nitrates.**—Treated with strong  $H_2SO_4$  and  $Cu$  turnings give off  $NO$ , which forms orange red  $NO_2$  with air. A better test is to mix in a test tube with a concentrated solution of  $FeSO_4$ . Add strong  $H_2SO_4$  in the cold, letting it run down the side of the tube and collect at the bottom; where the two layers are in contact, a brown or black ring is formed.

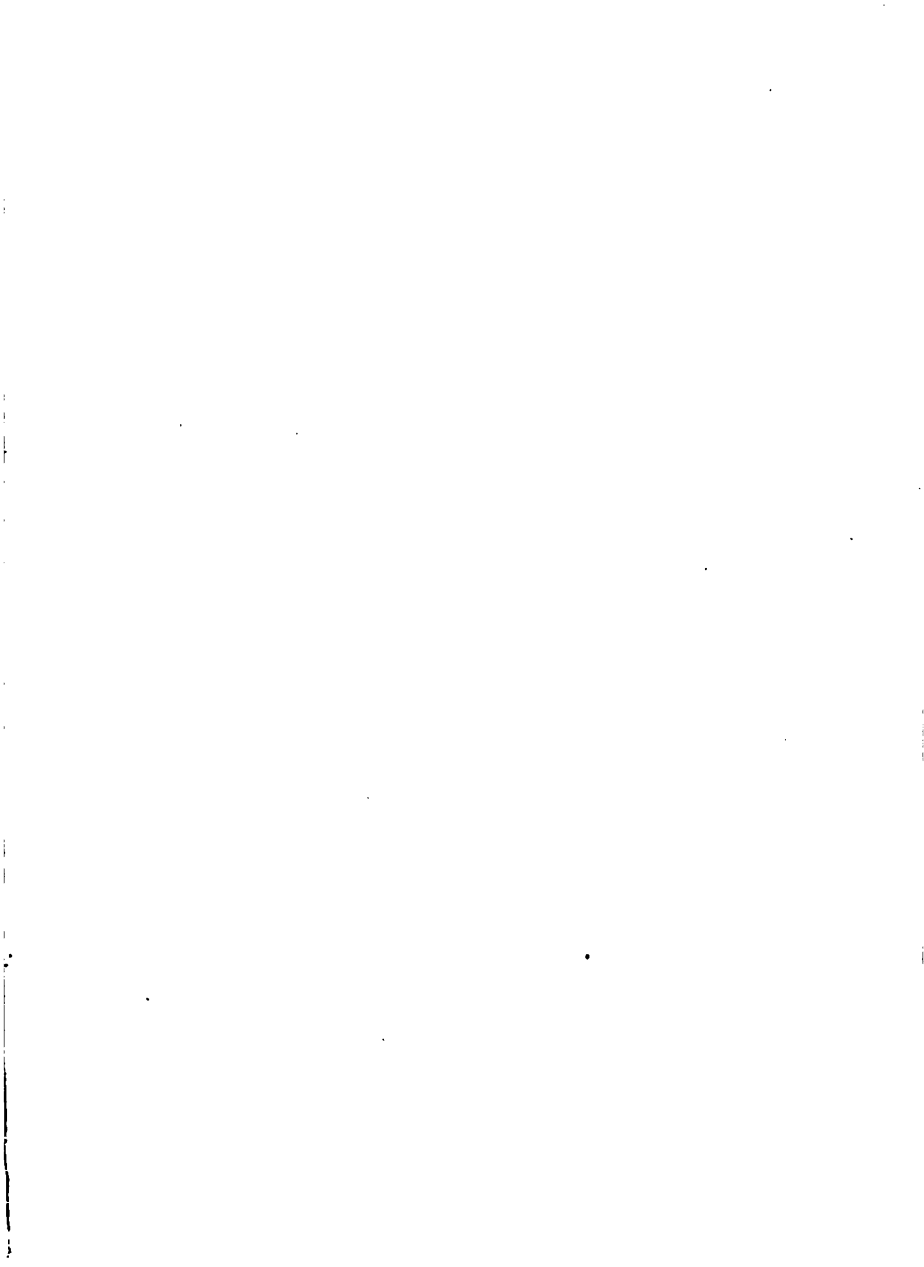
**Chlorates.**— $HCl + Aq$  or  $H_2SO_4$  decompose all salts, giving yellow solution and yellow green gas.

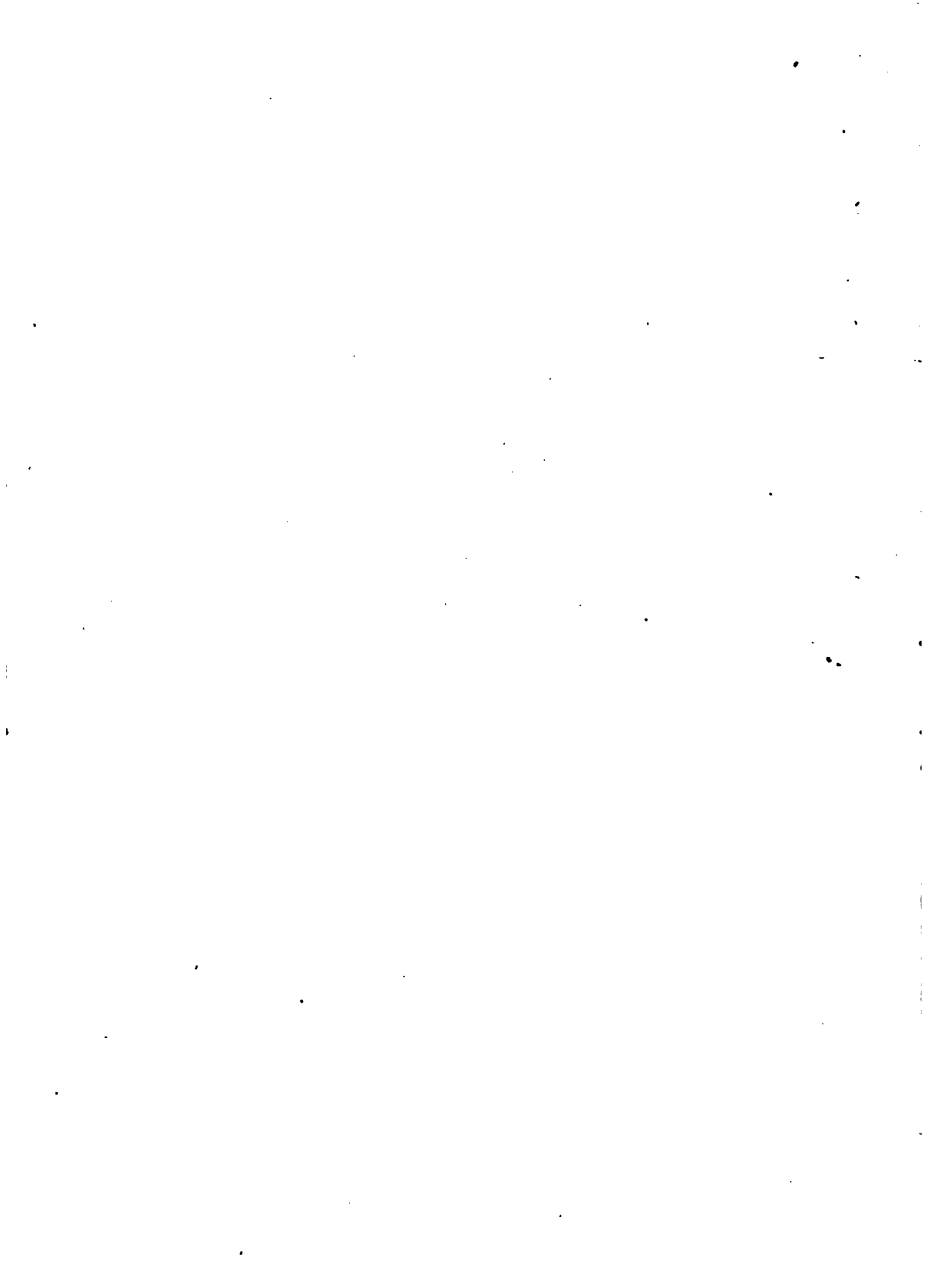
**Acetates.**— $\text{H}_2\text{SO}_4$  liberates  $\text{HC}_2\text{H}_3\text{O}_2$ , which may be recognized by its odor. A neutral solution of an acetate, on the addition in the cold of a few drops of  $\text{FeCl}_3$ , turns red from the formation of  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ . On boiling the red solution, a brown basic salt is thrown down and the liquid above is colorless. Before applying this test, the bases of Grs. III.–VI. must be removed, and the solution made strictly neutral.

Table showing the Solubility in Water and Acids of the more Common Salts.

	O.	H <sub>2</sub> S.	HCl.	HBr.	HI.	HON.	H <sub>2</sub> CrO <sub>4</sub> .	H <sub>2</sub> AsO <sub>3</sub> .	H <sub>2</sub> AsO <sub>4</sub> .	H <sub>2</sub> SO <sub>4</sub> .	H <sub>3</sub> PO <sub>4</sub> .	H <sub>3</sub> BO <sub>3</sub> .	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	HFL.	H <sub>2</sub> CO <sub>3</sub> .	H <sub>4</sub> SiO <sub>4</sub> .	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .	H <sub>4</sub> Fe(CN) <sub>6</sub> .	H <sub>4</sub> Fe <sub>2</sub> (CN) <sub>12</sub> .	HNO <sub>3</sub> .	HClO <sub>3</sub> .	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .	
K <sup>+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Na <sup>+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Ca <sup>2+</sup>	1-2	1	1	1	1	1	1	1	1	1-2	1	1	1	1	1	1	1	1	1	1	1	1	1
Ba <sup>2+</sup>	1-2	1	1	1	1	1	1	1	1	1-2	1	1	1	1	1	1	1	1	1	1	1	1	1
Al <sup>3+</sup>	1-2	1	1	1	1	1	1	1	1	1-2	1	1	1	1	1	1	1	1	1	1	1	1	1
Mg <sup>2+</sup>	1-2	1	1	1	1	1	1	1	1	1-2	1	1	1	1	1	1	1	1	1	1	1	1	1
Fe <sup>2+</sup>	1-2	1	1	1	1	1	1	1	1	1-2	1	1	1	1	1	1	1	1	1	1	1	1	1
Zn <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mn <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Ni <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Co <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Ag <sup>+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Pb <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Hg <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Bi <sup>3+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Cu <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Sn <sup>2+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Bu <sup>+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Sn <sup>4+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Pb <sup>4+</sup>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

1 = soluble in water; 2 = soluble in acids only; 3 = insoluble in water or acids; 1-2 = sparingly soluble in water, readily in acids; 1-3 = sparingly soluble in water and acids; 2-3 = sparingly soluble in acids only.





JAN 2 1908

JUN 10 1908

OCT 10 1908

SEP 17 1908

DEC 14 1908

JUL 25 1910

JAN 11 1909

FEB 20 1909

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